

Supporting Information for

**Novel chiral Schiff base/Ti(IV) Catalysts for the Catalytic Asymmetric
Epoxidation of *N*-Alkenyl Sulfonamides**

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1. General

Unless otherwise noted, all the starting materials and reagents were purchased from commercial suppliers and used without further purification. Solvents were purified by standard procedures. CH₂Cl₂, acetone and Toluene and xylene and *o*, *m*, *p*-xylene were freshly distilled prior to use. Reactions were monitored by thin layer chromatography (TLC) and analysis of TLCs was done either via UV light (254 nm) or pma (phosphomolybdic acid). Melting points were determined by using a standard melting point apparatus and were uncorrected. NMR spectra were recorded as CDCl₃ solution on 400 MHz instrument. The ¹H NMR chemical shifts are reported as δ value in parts per million (ppm) relative to tetramethylsilane (TMS, δ = 0.00)/CHCl₃ (δ = 7.26) as internal standard. The ¹³C NMR chemical shifts are reported as δ values in parts per million (ppm) downfield from TMS and referenced with respect to the CDCl₃ signal (triplet, centerline δ = 77.0 ppm). High-resolution mass spectra (HRMS) were measured with ESI. IR spectra were recorded as KBr disks. The yields are of materials isolated by column chromatography on silica gel plates, and column chromatography purifications were carried out using silica gel GF254. Specific rotation was determined by Rudolph Research Analytical Autopol IV Polarimeter. Enantiomeric excess (ee) determination was carried out on an Agilent 1260 interfaced to a HP 71 series computer workstation with Chiralpak AD/OD-H column.

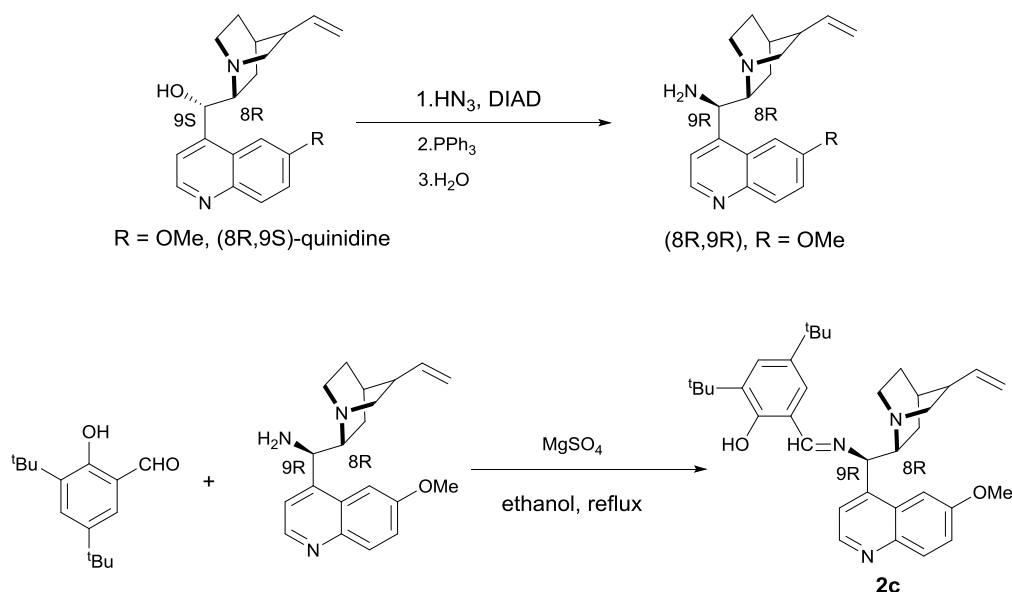
2. General procedure for the preparation of chiral Schiff base ligands

The ligands **2a-2b** were synthesized according to our previous report.¹

The *cinchona* alkaloids were transformed into corresponding 9-amino compounds, followed by condensation with different 3,5-Bis(1,1-dimethylethyl)-2-hydroxy-benzaldehyde to give the corresponding Schiff bases **2c-2f**. Preparation of the ligands with **2c** as example:

(8*R*,9*R*)-9-amino-(9-deoxy)-epiquinidine was prepared according to the literatures.² Dissolved

(8*R*,9*R*)-9-amino-(9-deoxy)-epiquinidine (646.8 mg, 2.0 mmol) and 3,5-di-*tert*-butylsalicylaldehyde (515.5 mg, 2.2 mmol) in absolute ethanol (30 mL), then the reaction was heated to reflux. After that, 3 g MgSO₄ (dried at 110°C for 3 h before use) was added to the solution. After 5 h, the mixture was slowly cooled down to room temperature and filtrated. The solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel (CH₂Cl₂/ methanol 80:1 to 60:1) to afford the Schiff base ligand **2c** as a yellow solid (970.5 mg, 90% yield).



Scheme 1. Procedure for the preparation of **2c**

2d-2f were synthesized following the similar procedures. **2d** was using cinchonine, while **2e** was using quinine and **2f** was using hydroquinine as the starting material.

3. Characterization data for new chiral Schiff base ligands

Catalyst 2c: Yellow solid; 90% yield; m.p. 105-107 °C; $[\alpha]_D^{20} +72$ (*c* 0.25, CHCl₃); IR (KBr): $\nu_{\max} = 3429, 2950, 2869, 1620, 1278 \text{ cm}^{-1}$; ¹H NMR (400 MHz, CDCl₃): $\delta = 13.5$ (s, 1H), 8.77 (d, *J* = 4.4 Hz, 1H), 8.41 (s, 1H), 8.04 (d, *J* = 9.2 Hz, 1H), 7.63 (br s, 1H), 7.51 (d, *J* = 4 Hz, 1H), 7.40 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.33 (d, *J* = 2.4 Hz, 1H), 7.06 (d, *J* = 2.4 Hz, 1H), 5.93-5.84 (m, 1H), 5.09-5.05 (m, 2H), 4.92 (br s, 1H), 4.04 (s, 3H), 3.54-3.45 (m, 1H), 3.08-2.97 (m, 2H), 2.95-2.90 (m, 2H), 2.31-2.25 (m, 1H), 1.64 (br s, 1H), 1.56-1.52 (m, 2H), 1.41 (s, 9H), 1.26 (s, 9H), 1.22-1.19 (m, 1H), 1.03-0.96 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.7, 157.9, 147.7, 145.0, 144.7, 140.4, 140.1, 136.4, 132.0, 127.7, 127.1, 126.4, 121.9, 121.2, 117.8, 114.6, 101.7, 60.9, 55.5, 49.6, 47.5, 39.5, 34.9, 34.1, 31.4$ (×3), 31.3, 29.4 (×3), 29.2, 27.8, 26.5, 24.9 ppm; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for C₃₅H₄₆N₃O₂ 540.3590, found 540.3599.

Catalyst **2d**: Yellow solid; 75% yield; m.p. 147-149 °C; $[\alpha]_D^{20}$ +85.5 (c 0.25, CHCl₃); IR (KBr): $\nu_{\max}$ = 3427, 3951, 2869, 1627, 1272 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 13.4 (s, 1H), 8.95 (d, *J* = 4.4 Hz, 1H), 8.42 (s, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.77-7.73 (m, 1H), 7.67-7.65 (m, 2H), 7.34-7.32 (m, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 5.89-5.81 (m, 1H), 5.14 (br s, 1H), 5.09-5.04 (m, 2H), 3.50-3.43 (m, 1H), 3.08-2.87 (m, 4H), 2.30-2.24 (m, 1H), 1.62 (br s, 1H), 1.56-1.53 (m, 2H), 1.41 (s, 9H), 1.26 (s, 9H), 1.22-1.19 (m, 2H), ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 197.3, 166.7, 157.9, 150.3, 148.6, 146.4, 140.4, 140.0, 136.4, 131.9, 130.7, 129.2, 127.8, 127.1, 126.9, 126.8, 126.4, 123.0, 120.6, 117.8, 114.6, 61.4, 49.6, 47.6, 39.6, 34.9, 34.0, 31.4, 31.3, 29.4, 29.2, 27.9, 26.4, 24.8 ppm; HRMS-ESI (*m/z*): [M+H]⁺ calcd for C₃₄H₄₄N₃O 510.3484, found 510.3493.

Catalyst **2e**: Red solid; 65% yield; m.p. 173-175 °C; $[\alpha]_D^{20}$ -96 (c 0.25, CHCl₃); IR (KBr): $\nu_{\max}$ = 3443, 2950, 2866, 1620, 1249, cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 13.3 (s, 1H), 8.78 (d, *J* = 4.8 Hz, 1H), 8.10 (d, *J* = 8.8 Hz, 2H), 7.63-7.57 (m, 2H), 7.42 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.31 (d, *J* = 2 Hz, 1H), 7.04 (d, *J* = 2 Hz, 1H), 4.67 (d, *J* = 9.2 Hz, 1H), 3.86-3.79 (m, 1H), 3.34-3.27 (m, 1H), 2.89-2.80 (m, 1H), 2.62-2.55 (m, 1H), 2.40-2.39 (m, 1H), 2.35-2.26 (m, 1H), 1.61 (br s, 1H), 1.51 (d, *J* = 6.4 Hz, 3H), 1.42 (s, 1H), 1.35 (s, 9H), 1.23 (s, 9H), 1.17-1.33 (m, 1H), 1.09-1.07 (m, 2H), 0.71-0.66 (m, 1H), ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 197.3, 166.4, 157.8, 157.1, 146.3, 142.7, 140.5, 136.4, 131.9, 131.0, 129.0, 128.5, 128.2, 127.5, 126.4, 123.1, 120.7, 117.6, 58.0, 16.8, 44.9, 40.4, 34.9, 34.1, 31.5, 31.3, 29.4, 29.2, 27.7, 25.3, 25.1, 24.6, 23.3, 14.7 ppm; HRMS-ESI (*m/z*): [M+H]⁺ calcd for C₃₄H₄₄N₃O₂ 526.3434, found 526.3415.

Catalyst **2f**: Yellow solid; 85% yield; m.p. 119-120 °C; $[\alpha]_D^{20}$ -86 (c 0.25, CHCl₃); IR (KBr): $\nu_{\max}$ = 3425, 2954, 2869, 1620, 1249 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 13.5 (s, 1H), 8.77 (d, *J* = 4.4 Hz, 1H), 8.42 (s, 1H), 8.05 (d, *J* = 9.2 Hz, 1H), 7.66 (br s, 1H), 7.49 (d, *J* = 4 Hz, 1H), 7.40 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.32 (d, *J* = 2 Hz, 1H), 7.04 (d, *J* = 2 Hz, 1H), 4.87 (d, *J* = 8.8 Hz, 1H), 4.03 (s, 3H), 3.60 (d, *J* = 8.8 Hz, 1H), 3.52 (d, *J* = 4.8 Hz, 1H), 3.23-3.17 (m, 2H), 2.82-2.76 (m, 1H), 2.51 (d, *J* = 13.6 Hz, 1H), 1.61 (s, 2H), 1.41 (s, 9H), 1.26 (s, 9H), 0.90-0.84 (m, 3H), 0.82-0.79 (m, 3H), 0.08 (s, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ = 166.4, 157.9, 147.6, 144.6, 140.1, 136.4, 132.0, 127.7, 127.1, 126.4, 121.7, 117.9, 102.0, 65.1, 60.5, 58.0, 55.5, 42.0, 40.9, 37.5, 34.9, 34.0, 31.4, 30.1, 29.4, 29.1, 28.9, 27.7, 25.7, 25.5, 23.3, 23.1, 14.1, 12.1, 11.2 ppm; HRMS-ESI (*m/z*): [M+H]⁺ calcd for C₃₅H₄₈N₃O₂ 542.3747, found 542.3746.

4. Effects of additives, concentration and oxidant on the 2f catalyzed asymmetric epoxidation of *N*-alkenyl sulfonamides

For the asymmetric catalytic reactions, the additives sometimes have shown positive effect for both yield and ee value. Hence, a series of additives were tested in the reactions (Table 1). Yamamoto³ had noted that magnesium oxide could both improve the reactivity and enantioselectivity significantly in the Hf(*Ot*-Bu)₄-BHA catalyzed epoxidation of *N*-alkenyl sulfonamides and the mechanism of MgO is still elusive. So, we also examined MgO in our reaction system, but it was inferior to Na₂CO₃ (Table 1, entry 1 vs. 2). Then other carbonates

were tested as additives (Table 1, entries 3-5), and K₂CO₃ gave better result. When the amount of K₂CO₃ was increased to 40 mol%, both the ee value and yield were improved (Table 1, entry 6). It is reported that the molecular sieve has shown an improvement in Ti-catalysed epoxidation of allylic alcohol.⁴ However, in this transformation, both 3 Å and 4 Å molecular sieve were not favorable (Table 1, entries 7& 8). Different concentration of 0.05 M, 0.1 M and 0.2 M were also tested, and the result showed that the 0.1 M was the best (Table 1, entry 6 vs. 9, 10). Two other commonly used oxidants were also been tested, and the results showed that TBHP (*t*-butyl hydroperoxide) almost could not oxidize the model reaction (Table 1, entry 11), while *m*-CPBA (3-chloroperoxybenzoic acid) could oxidize this reaction well but with racemic product (Table 1, entry 12).

Table 1. Effects of additives, concentration and oxidant on the 2f catalyzed asymmetric epoxidation of *N*-alkenyl sulfonamides

Reaction scheme: **1a** (allyl sulfonamide) $\xrightarrow[\text{toluene, 20-40 mol\% additive, oxidant (2.5 equiv.), rt, 72 h}]{10 \text{ mol\% Ti(Oi-Pr)}_4, 10 \text{ mol\% 2f}}$ **3a** (epoxide sulfonamide)

Entry ^a	Additive	Loading of base (mol%)	Conc.(M)	Oxidant	Yield ^b (%)	ee ^c (%)
1	MgO	20	0.1	CHP	42	65
2	Na ₂ CO ₃	20	0.1	CHP	44	69
3	NaHCO ₃	20	0.1	CHP	40	62
4	Cs ₂ CO ₃	20	0.1	CHP	50	55
5	K ₂ CO ₃	20	0.1	CHP	49	71
6	K ₂ CO ₃	40	0.1	CHP	56	74
7	3 Å MS	20	0.1	CHP	35	32
8	4 Å MS	20	0.1	CHP	30	35

9	K ₂ CO ₃	40	0.05	CHP	40	65
10	K ₂ CO ₃	40	0.2	CHP	58	62
11	K ₂ CO ₃	40	0.1	TBHP	trace	—
12	K ₂ CO ₃	40	0.1	<i>m</i> -CPBA	56	5

^a All reaction were performed with **1a** (0.20 mmol), Ti(O*i*-Pr)₄ (10 mol%) and catalyst **2f** (10 mol%), additive (20-40 mol%), oxidant (2.5 equiv.) in toluene (1-4 mL) at room temperature.

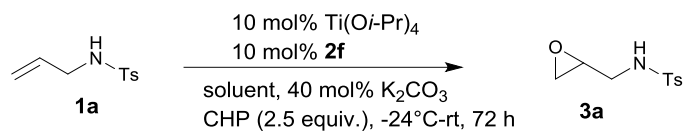
^b Isolated yield; reaction for 72 h.

^c Enantiomeric excess of **3a**, determined by chiral HPLC analysis using Chiralcel OD-H column.

5. Screening the solvents and the temperature in the asymmetric epoxidation of *N*-alkenyl sulfonamides

Solvent always plays an important role in the asymmetric catalysis. From Table 2, we can see that, when THF, DCM and acetone were tested, no significant results were obtained (Table 2, entries 1-3). The xylene gave better results than toluene. The ee value was increased and at the same time the reaction yield hold steady (Table 2, entry 5 vs 4). Interestingly, *o*, *m*, *p*-xylene gave different performance (Table 2, entries 6-8). When the *o*-xylene was used, the ee value had further increased to 83%, and the yield also increased proportionally (Table 2, entry 6). Hence, the *o*-xylene was the choice of solvent in the next experimental phase. When the temperature was decreased to 0°C, the ee valued increased significantly, but the yield decreased subtly. (Table 2, entry 9). As temperature was lowered around -10°C, the yield was decreased substantially with lightly increased ee value (Table 2, entry 10). When temperature reached below -24°C, both the yield and the ee value decreased potentially (Table 2, entry 11).

Table 2. Screening the solvents and the temperature in the asymmetric epoxidation of *N*-alkenyl sulfonamides



Entry ^a	Solvent	Temp. ($^\circ\text{C}$)	Yield ^b (%)	ee ^c (%)
1	DCM	rt	65	21
2	THF	rt	55	33
3	acetone	rt	45	45
4	toluene	rt	56	74
5	xylene	rt	60	77
6	<i>o</i> -xylene	rt	64	83
7	<i>m</i> -xylene	rt	56	73
8	<i>p</i> -xylene	rt	62	70
9	<i>o</i> -xylene	0	51	91
10	<i>o</i> -xylene	-10	28	92
11	<i>o</i> -xylene	-24	10	5

^a All reaction were performed with **1a** (0.20 mmol), $\text{Ti}(\text{O}i\text{-Pr})_4$ (10 mol%) and ligand **2f** (10 mol%), K_2CO_3 (40 mol%), CHP (2.5 equiv.) in different solvents (2 mL) in different reaction temperature.

^b Isolated yield; reaction for 72 h.

^c Enantiomeric excess of **3a**, determined by chiral HPLC analysis using Chiralcel OD-H column.

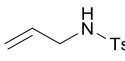
6. Typical catalytic asymmetric epoxidation of *N*-alkenyl sulfonamides under optimization conditions

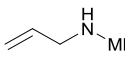
$\text{Ti}(\text{O}i\text{-Pr})_4$ (1.0 M in toluene, 0.02 mmol, 20 μL), Schiff base ligand **2f** (0.02 mmol, 10.8 mg) were dissolved in *o*-xylene (2 mL) at room temperature. The mixture was stirred at room temperature for 5 h. Then, the corresponding *N*-Alkenyl Sulfonamide (0.20 mmol) and K_2CO_3 (11.0 mg, 0.08 mmol) and cumene hydroperoxide (97 μL , 0.5 mmol) were added sequentially

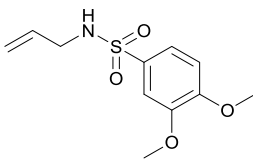
at 0 °C. The mixture was stirred for 72 h at 0°C, and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) to provide the desired product. The enantiomeric purity of the product was determined by HPLC analysis. The absolute configurations of the products were assigned by comparison to literature data.³

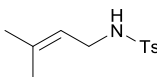
7. Characterization Data for Starting Materials and Products

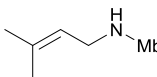
Characterization Data for Starting Materials:

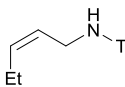
 **1a:** ¹H NMR (CDCl₃, 400MHz): δ = 7.77(d, *J* = 8.8 Hz, 2H), 7.33(d, *J* = 8.0 Hz, 2H), 5.79-5.69(m, 1H), 5.21-5.10(m, 2H), 4.45(br s, 1H), 3.61(t, *J* = 6 Hz, 2H), 2.45(s, 3H) ppm.

 **1b:** ¹H NMR (CDCl₃, 400MHz): δ = 7.81(d, *J* = 6.8Hz, 2H), 6.99-6.96(m, 2H), 5.75-5.67(m, 1H), 5.17-5.05(m, 2H), 4.92(br s, 1H), 3.87 (s, 3H), 3.56(s, 2H) ppm.

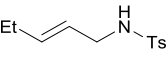
 **1c:** ¹H NMR (CDCl₃, 400MHz): δ = 7.51-7.49(m, 1H), 7.36(d, *J* = 6.0 Hz, 1H), 6.94(d, *J* = 8.8Hz, 1H), 5.77-5.67(m, 1H), 5.20-5.08(m, 2H), 4.82(br s, 1H), 3.93(s, 3H), 3.92(s, 3H), 5.58(s, 2H) ppm.

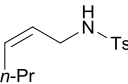
 **1d:** ¹H NMR (CDCl₃, 400MHz): δ = 7.76(d, *J* = 7.8 Hz, 2H), 7.33(d, *J* = 8.4 Hz, 2H), 5.04(s, 1H), 4.82(br s, 1H), 3.52(s, 2H), 2.42(s, 3H), 1.60(s, 3H), 1.52(s, 3H) ppm.

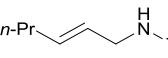
 **1e:** ¹H NMR (CDCl₃, 400MHz): δ = 7.76(m, 2H), 6.99-6.95(m, 2H), 5.07-5.01(m, 1H), 4.43(br s, 1H) 3.87(s, 3H), 3.51(t, *J* = 7.6Hz, 2H), 1.61(d, *J* = 11.6Hz, 3H), 1.52(d, *J* = 9.6Hz, 3H) ppm.

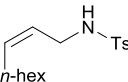
 **1f:** ¹H NMR (CDCl₃, 400MHz): δ = 7.77(d, *J* = 8.8Hz, 2H), 7.31(d, *J* = 8.2Hz, 2H), 5.20-5.43(m, 1H), 5.30-5.21(m, 1H), 4.85(br s, 1H), 3.60-3.57(m, 2H), 2.43(s, 3H) ,1.96-

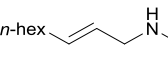
1.90(m, 2H), 0.89(t, $J = 7.2\text{Hz}$, 3H) ppm.

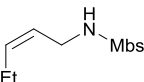
 **1g:** ^1H NMR (CDCl_3 , 400MHz): $\delta = 7.77(\text{d}, J = 8.4\text{Hz}, 2\text{H}), 7.33\text{-}7.30(\text{m}, 2\text{H}), 5.62\text{-}5.58(\text{m}, 1\text{H}), 5.32\text{-}5.27(\text{m}, 1\text{H}), 4.82(\text{br s}, 1\text{H}), 3.53\text{-}3.50(\text{m}, 2\text{H}), 2.43(\text{s}, 3\text{H}), 1.97\text{-}1.92(\text{m}, 2\text{H}), 0.93\text{-}0.87(\text{m}, 3\text{H})$ ppm.

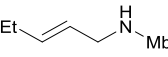
 **1h:** ^1H NMR (CDCl_3 , 400MHz): $\delta = 7.77(\text{d}, J = 8.8\text{Hz}, 2\text{H}), 7.30(\text{d}, J = 8.0\text{Hz}, 2\text{H}), 5.47\text{-}5.43(\text{m}, 1\text{H}), 5.28\text{-}5.27(\text{m}, 1\text{H}), 4.91(\text{br s}, 1\text{H}), 3.58(\text{t}, J = 6.4\text{Hz}, 2\text{H}), 2.42(\text{s}, 3\text{H}), 1.52(\text{dd}, J = 7.6, 14.8\text{Hz}, 2\text{H}), 1.32\text{-}1.28(\text{m}, 2\text{H}), 0.84\text{-}0.80(\text{m}, 3\text{H})$ ppm.

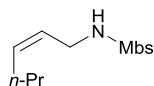
 **1i:** ^1H NMR (CDCl_3 , 400MHz): $\delta = 7.76(\text{d}, J = 8.4\text{Hz}, 2\text{H}), 7.29(\text{d}, J = 8.4\text{Hz}, 2\text{H}), 5.56\text{-}5.48(\text{m}, 1\text{H}), 5.32\text{-}5.27(\text{m}, 1\text{H}), 5.02(\text{br s}, 1\text{H}), 3.50(\text{d}, J = 6.0\text{Hz}, 2\text{H}), 2.41(\text{s}, 3\text{H}), 1.90\text{-}1.85(\text{m}, 2\text{H}), 1.29\text{-}1.24(\text{m}, 2\text{H}), 0.83\text{-}0.79(\text{m}, 3\text{H})$ ppm.

 **1j:** ^1H NMR (CDCl_3 , 400MHz): $\delta = 7.77(\text{d}, J = 8.4\text{Hz}, 2\text{H}), 7.30(\text{d}, J = 8.0\text{Hz}, 2\text{H}), 5.49\text{-}5.42(\text{m}, 1\text{H}), 5.29\text{-}5.23(\text{m}, 1\text{H}), 4.94(\text{br s}, 1\text{H}), 3.58(\text{t}, J = 6.4\text{Hz}, 2\text{H}), 2.42(\text{s}, 3\text{H}), 1.92\text{-}1.87(\text{m}, 2\text{H}), 1.27\text{-}1.21(\text{m}, 8\text{H}), 0.82(\text{t}, J = 6.4\text{Hz}, 3\text{H})$ ppm.

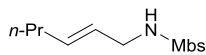
 **1k:** ^1H NMR (CDCl_3 , 400MHz): $\delta = 7.76(\text{d}, J = 8.4\text{Hz}, 2\text{H}), 7.31(\text{d}, J = 8.0\text{Hz}, 2\text{H}), 5.58\text{-}5.50(\text{m}, 1\text{H}), 5.33\text{-}4.70(\text{m}, 1\text{H}), 4.70(\text{br s}, 1\text{H}), 3.52(\text{t}, J = 6.4\text{Hz}, 2\text{H}), 2.43(\text{s}, 3\text{H}), 1.92\text{-}1.89(\text{m}, 2\text{H}), 1.28\text{-}1.23(\text{m}, 8\text{H}), 0.87(\text{t}, J = 6.8\text{Hz}, 3\text{H})$ ppm.

 **1l:** ^1H NMR (CDCl_3 , 400MHz): $\delta = 7.98(\text{d}, J = 8.4\text{Hz}, 2\text{H}), 7.50\text{-}7.43(\text{m}, 1\text{H}), 5.29\text{-}5.20(\text{m}, 1\text{H}), 4.81(\text{br s}, 1\text{H}), 3.87(\text{s}, 3\text{H}), 3.57(\text{t}, J = 6.4\text{Hz}, 2\text{H}), 1.98\text{-}1.90(\text{m}, 2\text{H}), 0.90(\text{t}, J = 7.6\text{Hz}, 3\text{H})$ ppm.

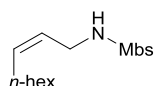
 **1m:** ^1H NMR (CDCl_3 , 400MHz): $\delta = 7.80(\text{d}, J = 8.8\text{Hz}, 2\text{H}), 6.99(\text{d}, J = 8.4\text{Hz}, 2\text{H}), 5.62\text{-}5.56(\text{m}, 1\text{H}), 5.33\text{-}5.26(\text{m}, 1\text{H}), 4.58(\text{br s}, 1\text{H}), 3.87(\text{s}, 3\text{H}), 3.51(\text{t}, J = 5.6\text{Hz}, 2\text{H}), 1.97\text{-}1.93(\text{m}, 2\text{H}), 0.90(\text{t}, J = 7.6\text{Hz}, 3\text{H})$ ppm.



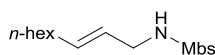
1n: ^1H NMR (CDCl_3 , 400MHz): δ = 7.82(d, J = 8.4Hz, 2H), 6.98(d, J = 8.4Hz, 2H), 5.50-5.44(m, 1H), 5.31-5.25(m, 1H), 4.79(br s, 1H), 3.87(s, 3H), 3.57(t, J = 6.4Hz, 2H), 1.92-1.87(m, 2H), 1.32-1.25(m, 2H), 0.84-0.80(m, 3H) ppm.



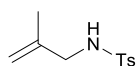
1o: ^1H NMR (CDCl_3 , 400MHz): δ = 7.81(d, J = 8.8Hz, 2H), 7.98(d, J = 8.8Hz, 2H), 5.59-5.51(m, 1H), 5.36-5.26(m, 1H), 4.59(br s, 1H), 3.88(s, 3H), 3.52(d, J = 5.2Hz, 2H), 1.92-1.91(m, 2H), 1.34-1.28(m, 2H), 0.87-0.82(m, 3H) ppm.



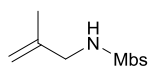
1p: ^1H NMR (CDCl_3 , 400MHz): δ = 7.83(d, J = 8.8Hz, 2H), 7.31(d, J = 8.0Hz, 2H), 5.52-5.45(m, 1H), 5.30-5.24(m, 1H), 4.63(br s, 1H), 3.88(s, 3H), 3.58(t, J = 5.6Hz, 2H), 1.94-1.89(m, 2H), 1.28-1.27 (m, 8H) , 0.89-0.85(m, 3H) ppm.



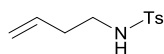
1q: ^1H NMR (CDCl_3 , 400MHz): δ = 7.81(d, J = 9.2Hz, 2H), 6.98(d, J = 9.2Hz, 2H), 5.61-5.51(m, 1H), 5.33-5.24(m, 1H), 4.66(br s, 1H), 3.87(s, 3H), 3.51(t, J = 6.0Hz, 2H), 1.93-1.91(m, 2H), 1.28-1.23 (m, 8H) , 0.89-0.85(m, 3H) ppm.



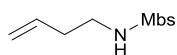
1r: ^1H NMR (CDCl_3 , 400MHz): δ = 7.77(d, J = 8.4Hz, 2H), 7.32(d, J = 8.0Hz, 2H), 4.86(d, J = 14.8Hz, 2H), 4.67(br s, 1H), 3.45(d, J = 3.6Hz, 2H), 2.45(s, 3H), 1.69(s, 3H) ppm.



1s: ^1H NMR (CDCl_3 , 400MHz): δ = 7.82-7.79 (m, 2H) , 6.99-6.95(m, 2H), 4.85-4.79(m, 2H), 3.87(s, 3H), 3.46(s, 2H), 1.67(d, J = 7.2 Hz, 3H) ppm.

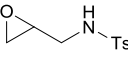


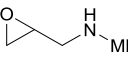
1t: ^1H NMR (CDCl_3 , 400MHz): δ = 7.75(d, J = 8.4 Hz, 2H) 7.31(d, J = 8.4 Hz, 2H), 5.67-5.57(m, 1H), 5.07-5.00(m, 2H), 4.64(br s, 1H), 3.01(d, J = 6.4Hz, 2H), 2.45(s, 3H), 2.20(d, J = 6.8 Hz, 2H) ppm.

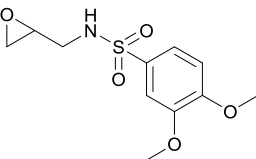


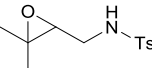
1u: ^1H NMR (CDCl_3 , 400MHz): δ = 7.81(d, J = 8.6 Hz, 2H), 7.99(d, J = 7.6 Hz, 2H), 5.87-5.58(m, 1H), 5.08-5.01(m, 2H), 4.66(br s, 1H), 3.88(s, 3H), 3.03-2.99(m, 2H), 2.21(d, J = 6.8Hz, 2H) ppm.

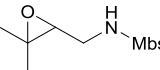
Characterization Data for Products:

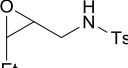
 **3a(R):** ^1H NMR (CDCl_3 , 400MHz): δ = 7.74 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8 Hz, 2H), 4.85 (br s, 1H), , 3.35-3.30 (m, 1H), 3.05-3.01 (m, 2H), 2.76-2.74 (m, 1H), 2.64-2.62 (m, 1H), 2.43 (s, 3H) ppm; $[\alpha]_D^{20}$ +13.1 (c 0.25, CHCl_3).

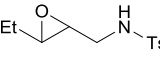
 **3b:** ^1H NMR (CDCl_3 , 400MHz): δ = 7.80 (d, J = 9.2Hz, 2H), 6.98 (d, J = 8.8Hz, 2H), 4.95-4.72 (m, 1H), 3.87 (s, 3H), 3.35-3.29 (m, 1H), 3.07-2.99 (m, 2H) , 2.76 (t, J = 4.4Hz, 1H), 2.64-2.63 (m, 1H) ppm; $[\alpha]_D^{20}$ +9.3 (c 0.25, CHCl_3).

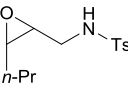
 **3c:** ^1H NMR (CDCl_3 , 400MHz): δ = 7.48 (d, J = 6 Hz, 1H), 7.32 (d, J = 2.4 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 4.82 (t, J = 6.4 Hz, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 3.38-3.32 (m, 1H), 3.09-3.06 (m, 1H), 3.05-2.99 (m, 1H), 2.78-2.76 (m, 1H), 2.66-2.64 (m, 1H) ppm; $[\alpha]_D^{20}$ +11.3 (c 0.25, CHCl_3).

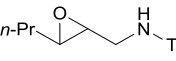
 **3d:** ^1H NMR (CDCl_3 , 400MHz): δ = 7.76 (d, J = 8 Hz, 2H), 7.31 (d, J = 8 Hz, 2H), 5.24 (br s, 1H), 3.27-3.23 (m, 1H), 3.00-2.95 (m, 1H), 2.88-2.85 (m, 1H), 2.42 (s, 3H), 1.26 (s, 3H), 1.21 (s, 3H) ppm; $[\alpha]_D^{20}$ +26.5 (c 0.50, CHCl_3).

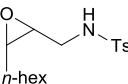
 **3e:** ^1H NMR (CDCl_3 , 400MHz): δ = 7.82 (d, J = 9.2 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 5.25 (br s, 1H), 3.87 (s, 3H), 3.25-3.21 (m, 1H), 3.01-2.96 (m, 1H), 2.88-2.85 (m, 1H), 1.27 (s, 3H), 1.22 (s, 3H) ppm; $[\alpha]_D^{20}$ +24.3 (c 0.50, CHCl_3).

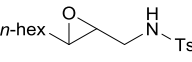
 **3f:** ^1H NMR (CDCl_3 , 400MHz): δ = 7.77 (d, J = 8 Hz, 2H), 7.31 (d, J = 8 Hz, 2H), 5.35-5.32 (m, 1H), 3.31-3.24 (m, 1H), 3.05-3.02 (m, 1H), 2.98-2.89 (m, 2H), 2.42 (s, 3H), 1.49-1.42 (m, 2H), 0.99 (t, J = 7.6 Hz, 3H) ppm; $[\alpha]_D^{20}$ +15.2 (c 0.25, CHCl_3).

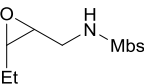
 **3g**: ^1H NMR (CDCl_3 , 400MHz): δ = 7.74 (d, J = 8 Hz, 2H), 7.31 (d, J = 8 Hz, 2H), 5.15 (br s, 1H), 3.29-3.23 (m, 1H), 3.05-2.98 (m, 1H), 2.86-2.84 (m, 1H), 2.81-2.79 (m, 1H), 2.42 (s, 3H), 1.56-1.50 (m, 2H), 0.95-0.91 (m, 3H) ppm; $[\alpha]_D^{20}$ +16.3 (c 0.25, CHCl_3).

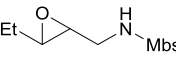
 **3h**: ^1H NMR (CDCl_3 , 400MHz): δ = 7.74 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8 Hz, 2H), 5.13 (br s, 1H), 3.33-3.27 (m, 1H), 3.05-2.99 (m, 1H), 2.98-2.93 (m, 2H), 2.44 (s, 3H), 1.49-1.39 (m, 4H), 0.95-0.92 (m, 3H) ppm; $[\alpha]_D^{20}$ +11.4 (c 1.0, CHCl_3).

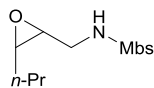
 **3i**: ^1H NMR (CDCl_3 , 400MHz): δ = 7.75 (d, J = 7.6 Hz, 2H), 7.32 (d, J = 3.6 Hz, 2H), 5.07 (br s, 1H), 3.28-3.25 (m, 1H), 3.05-3.01 (m, 1H), 2.83 (s, 2H), 2.43 (s, 3H), 1.46-1.39 (m, 4H), 0.94-0.91 (m, 3H) ppm; $[\alpha]_D^{20}$ +10.6 (c 0.50, CHCl_3).

 **3j**: ^1H NMR (CDCl_3 , 400MHz): δ = 7.77 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8 Hz, 2H), 5.17 (br s, 1H), 3.31-3.26 (m, 1H), 3.04-3.01 (m, 1H), 2.98-2.93 (m, 2H), 2.43 (m, 3H), 1.45-1.26 (m, 4H), 1.30-1.26 (m, 6H), 0.90-0.86 (m, 3H) ppm; $[\alpha]_D^{20}$ +13.9 (c 1.0, CHCl_3).

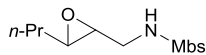
 **3k**: ^1H NMR (CDCl_3 , 400MHz): δ = 7.73 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8 Hz, 2H), 5.40 (br s, 1H), 3.27-3.23 (m, 1H), 3.00-2.97 (m, 1H), 2.82-2.79 (m, 2H), 3.00 (m, 3H), 1.34-1.23 (m, 10H), 0.89-0.83 (m, 3H) ppm; $[\alpha]_D^{20}$ +9.7 (c 0.5, CHCl_3).

 **3l**: ^1H NMR (CDCl_3 , 400MHz): δ = 7.86 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 5.17 (br s, 1H), 3.87 (s, 3H), 3.30-3.25 (m, 1H), 3.06-3.02 (m, 1H), 2.94-2.90 (m, 2H), 1.49-1.45 (m, 2H), 1.02-0.99 (m, 3H) ppm; $[\alpha]_D^{20}$ +10.5 (c 0.25, CHCl_3).

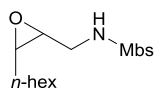
 **3m**: ^1H NMR (CDCl_3 , 400MHz): δ = 7.80 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 5.04 (br s, 1H), 3.87 (s, 3H), 3.27 (d, J = 14 Hz, 1H), 3.02 (d, J = 14 Hz, 1H), 2.84-2.81 (m, 2H), 1.57-1.52 (m, 2H), 0.97-0.93 (m, 3H) ppm; $[\alpha]_D^{20}$ +12.3 (c 0.25, CHCl_3).



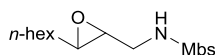
3n: ^1H NMR (CDCl_3 , 400MHz): δ = 7.82 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 4.71 (br s, 1H), 3.87 (s, 3H), 3.31-3.27 (m, 1H), 3.06-3.02 (m, 1H), 2.96-2.93 (m, 2H), 1.48-1.40 (m, 4H), 0.95-0.92 (m, 3H) ppm; $[\alpha]_D^{20}$ +13.7 (c 0.5, CHCl_3).



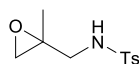
3o: ^1H NMR (CDCl_3 , 400MHz): δ = 7.79 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 5.01 (br s, 1H), 3.86 (s, 3H), 3.27 (d, J = 13.6 Hz, 1H), 3.06-2.95 (m, 1H), 2.84-2.93 (m, 2H), 1.49-1.39 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H) ppm; $[\alpha]_D^{20}$ +10.9 (c 0.25, CHCl_3).



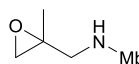
3p: ^1H NMR (CDCl_3 , 400MHz): δ = 7.82 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 5.13 (br s, 1H), 3.87 (s, 3H), 3.31-2.3.25 (m, 1H), 3.04-2.98 (m, 1H), 2.97-2.92 (m, 2H), 1.44-1.40 (m, 4H), 1.30-1.26 (m, 6H), 0.90-0.86 (m, 3H) ppm; $[\alpha]_D^{20}$ +15.7 (c 0.4, CHCl_3).



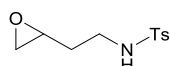
3q: ^1H NMR (CDCl_3 , 400MHz): δ = 7.79 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 5.05 (t, J = 6 Hz, 1H), 3.87 (s, 3H), 3.03-2.97 (m, 1H), 2.83-2.79 (m, 1H), 2.78-2.76 (m, 2H), 1.50-1.47 (m, 2H), 1.39-1.34 (m, 2H), 1.31-1.26 (m, 6H), 0.89-0.86 (m, 3H) ppm; $[\alpha]_D^{20}$ +12.2 (c 0.75, CHCl_3).



3r: ^1H NMR (CDCl_3 , 400MHz): δ = 7.73 (d, J = 8.4Hz, 2H), 7.31 (d, J = 8.0Hz, 2H), 5.01 (t, J = 6.4Hz, 1H), 3.12-3.10 (m, 2H), 2.83(d, J = 4.4Hz, 1H), 2.81 (d, J = 4.4Hz, 1H), 2.42 (s, 3H), 1.33 (s, 3H) ppm; $[\alpha]_D^{20}$ +17.1 (c 0.25, CHCl_3).

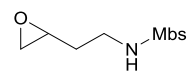


3s: ^1H NMR (CDCl_3 , 400MHz): δ = 7.73 (d, J = 8.8Hz, 2H), 6.95 (d, J = 8.8Hz, 2H), 5.01 (br s, 1H), 3.84 (s, 3H), 3.07 (d, J = 6.4Hz, 2H), 2.80 (d, J = 4.4Hz, 1H), 2.58 (d, J = 4.0Hz, 1H), 1.30 (s, 3H) ppm; $[\alpha]_D^{20}$ +8.2 (c 0.5, CHCl_3).



3t: ^1H NMR (CDCl_3 , 400MHz): δ = 7.76 (d, J = 8.0Hz, 2H), 7.32 (d, J = 8.0Hz, 2H), 5.19 (t, J = 6Hz, 1H), 3.09 (q, J = 6.4Hz, 2H), 2.96-2.92 (m, 1H), 2.74 (t, J = 4.4Hz, 1H), 2.48-2.46 (m, 1H), 2.43 (s, 3H), 1.96-1.88 (m, 1H), 1.59-1.52 (m, 1H) ppm; $[\alpha]_D^{20}$ +13.5

(c 0.25, CHCl₃).

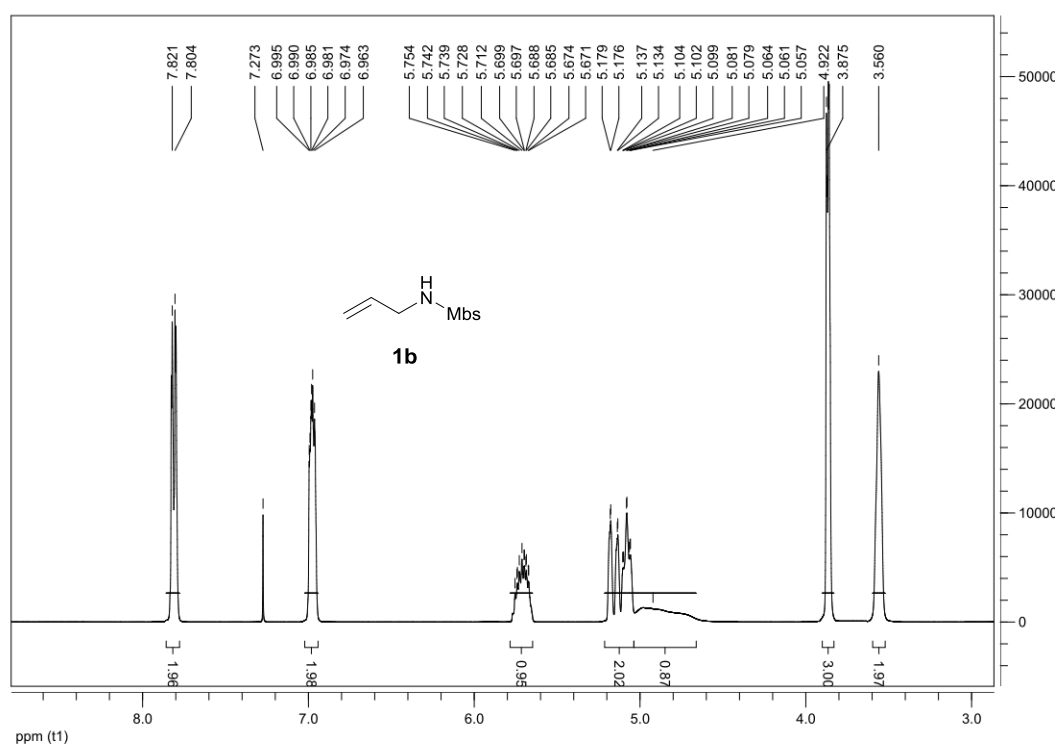
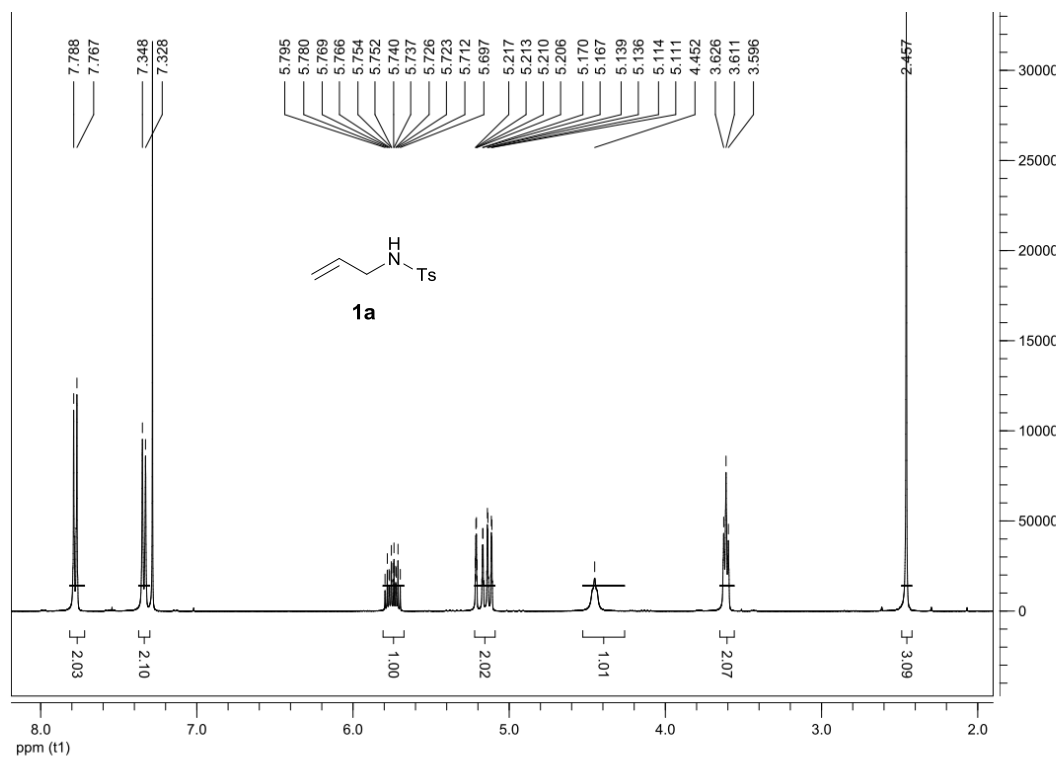


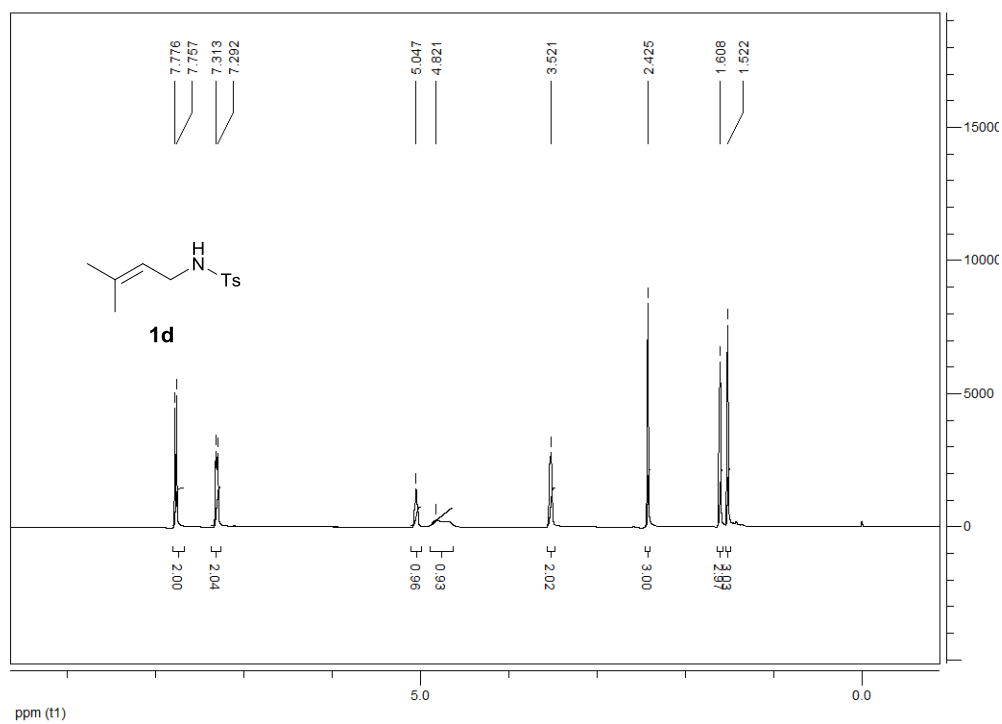
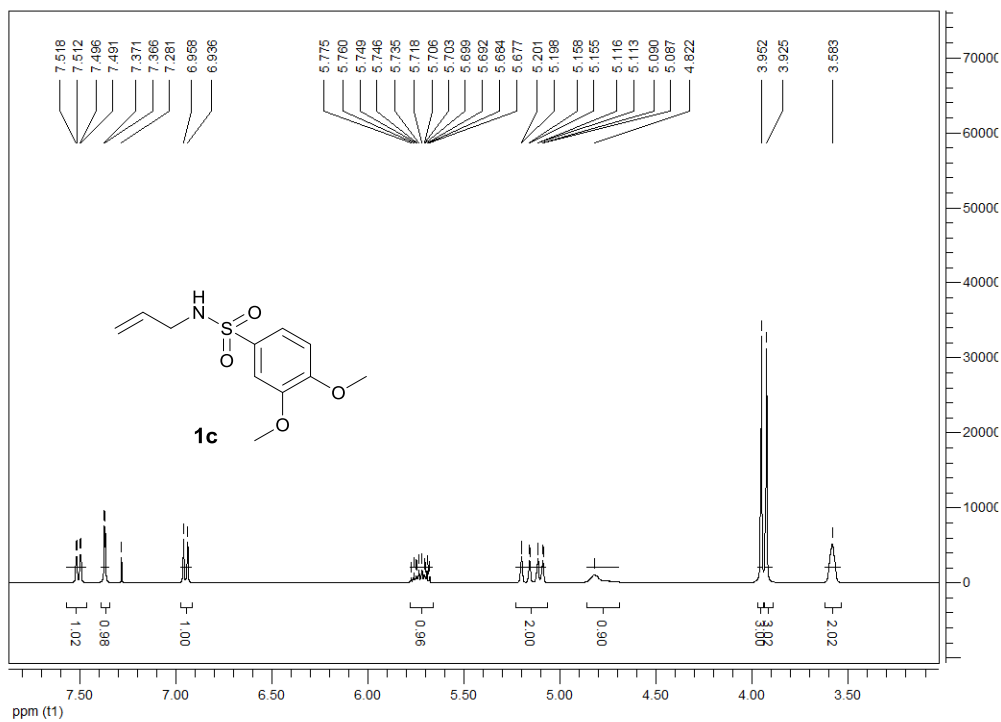
3u: ¹H NMR (CDCl₃, 400MHz): δ = 7.81 (d, *J* = 8.8Hz, 2H), 7.99 (d, *J* = 8.8Hz, 2H), 5.10 (br s, 1H), 3.87 (s, 3H), 3.10-3.07 (m, 2H), 2.94-2.93 (m, 1H), 2.75-2.72 (m, 1H), 2.49-2.46 (m, 1H), 1.94-1.90 (m, 1H), 1.58-1.53 (m, 1H) ppm; [α]_D²⁰ +12.9 (c 0.5, CHCl₃).

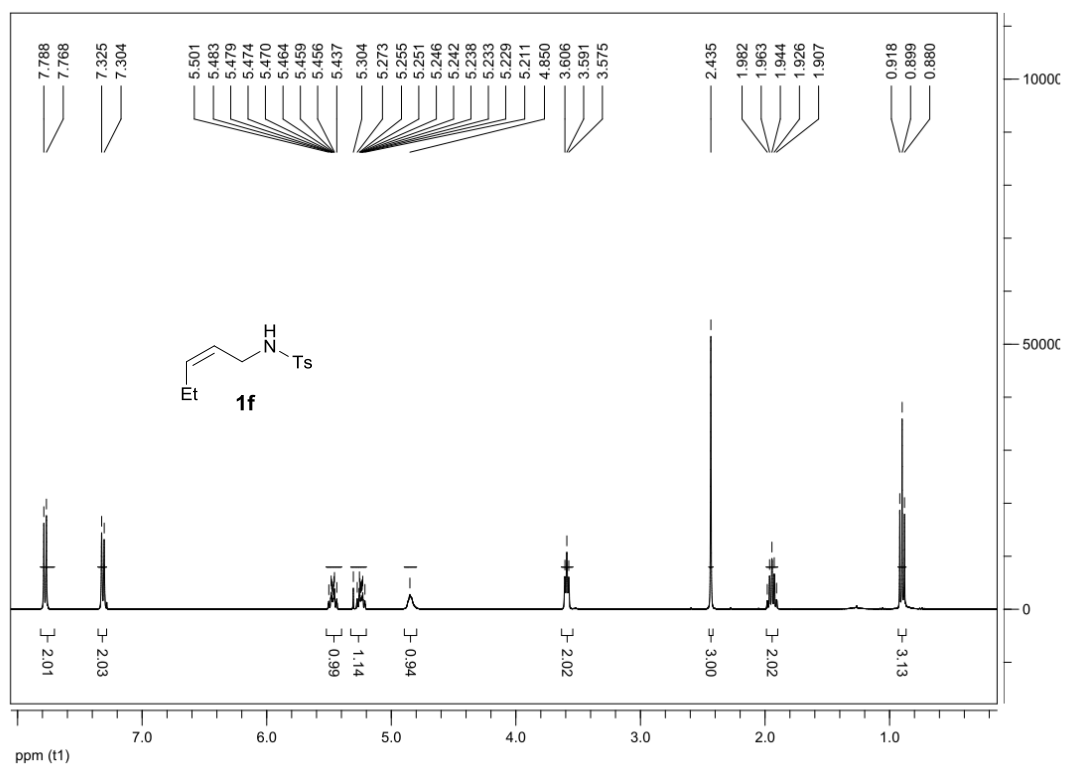
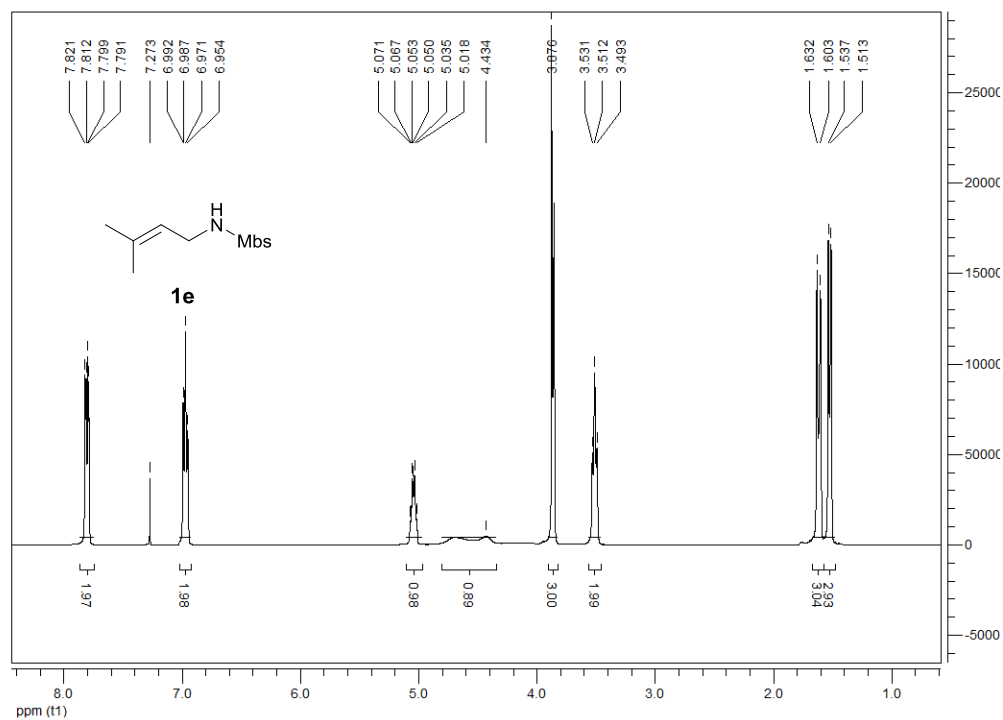
8. References

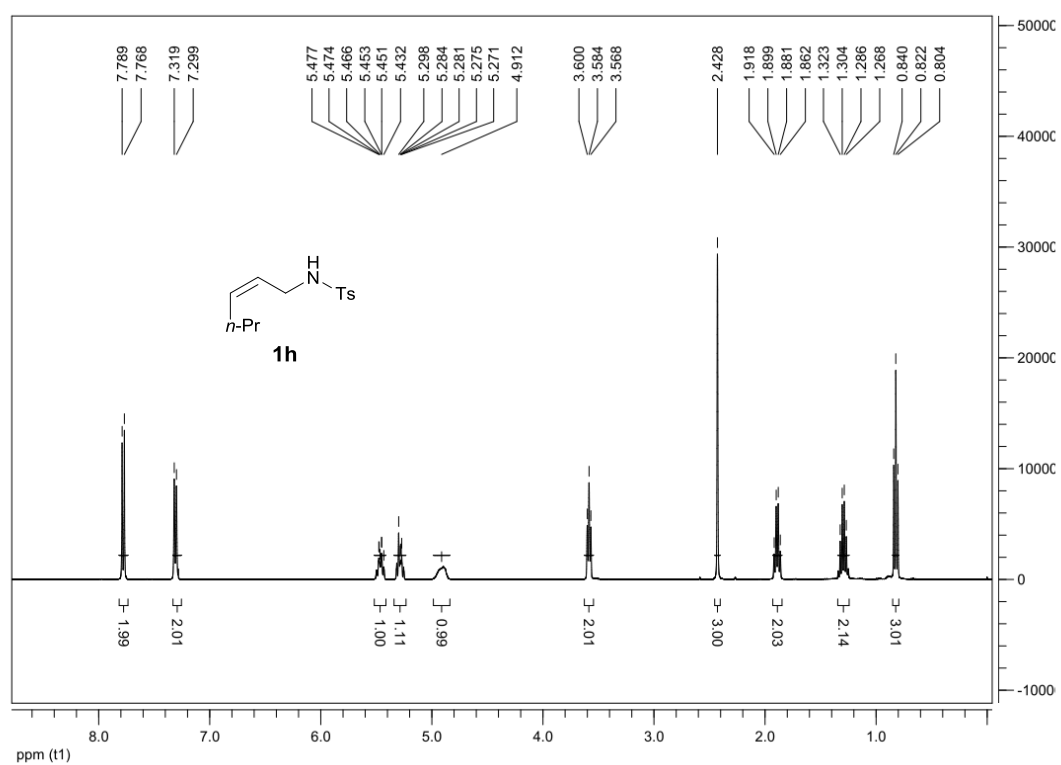
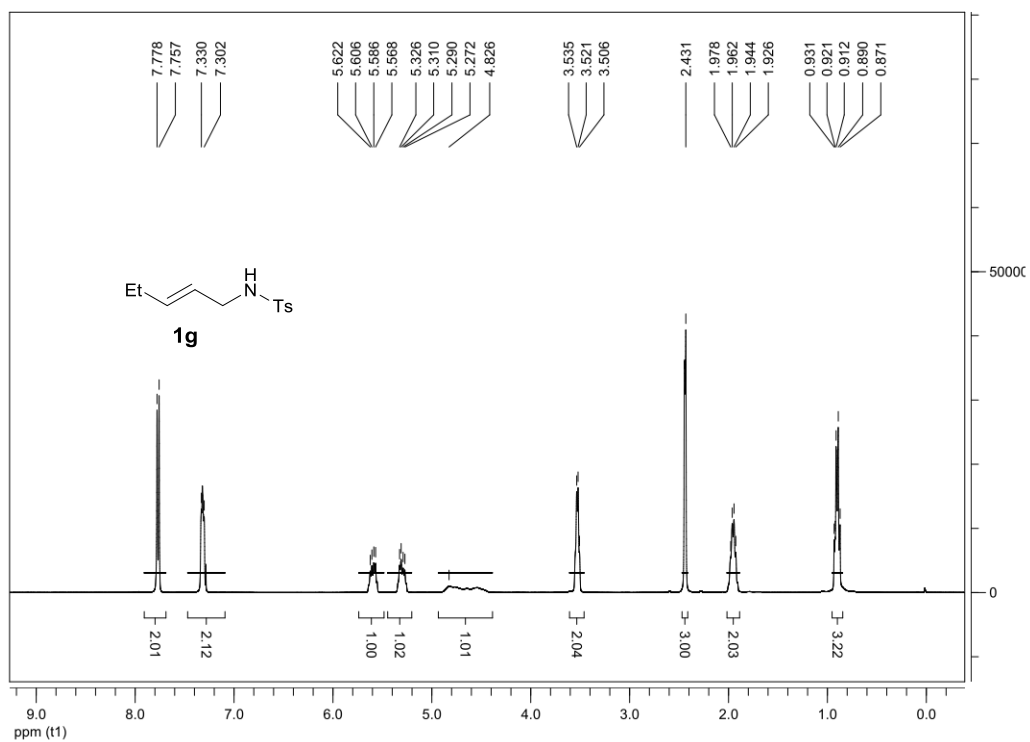
1. (a) Y. Wei, L. Yao, B.-L. Zhang, W. He and S.-Y. Zhang, *Tetrahedron* 2011, **67**, 8552-8558; (b) L. Yao, Y. Wei, P.-A. Wang, W. He and S.-Y. Zhang, *Tetrahedron* 2012, **68**, 9119-9124.
2. (a) B. Henri, B. Jürgen and N. Bernhard, *Tetrahedron: Asymmetry* 1995, **6**, 1699-1702; (b) J. F. Larrow and E. N. Jacobsen, *J. Org. Chem.*, 1994, **59**, 1939-1942; (c) W. He, P. Liu, B.-L. Zhang, X.-L. Sun and S.-Y. Zhang, *Appl. Organomet. Chem.*, 2006, **20**, 328-334.
3. J. L. Olivares-Romero, Z. Li and H. Yamamoto, *J. Am. Chem. Soc.*, 2012, **134**, 5440-5443.
4. Y. Gao, R. M. Hanson, J. M. Klunder, S. Y. KO, H. Masamune and K. B. Sharpless, *J. Am. Chem. Soc.*, 1987, **109**, 5765-5780.

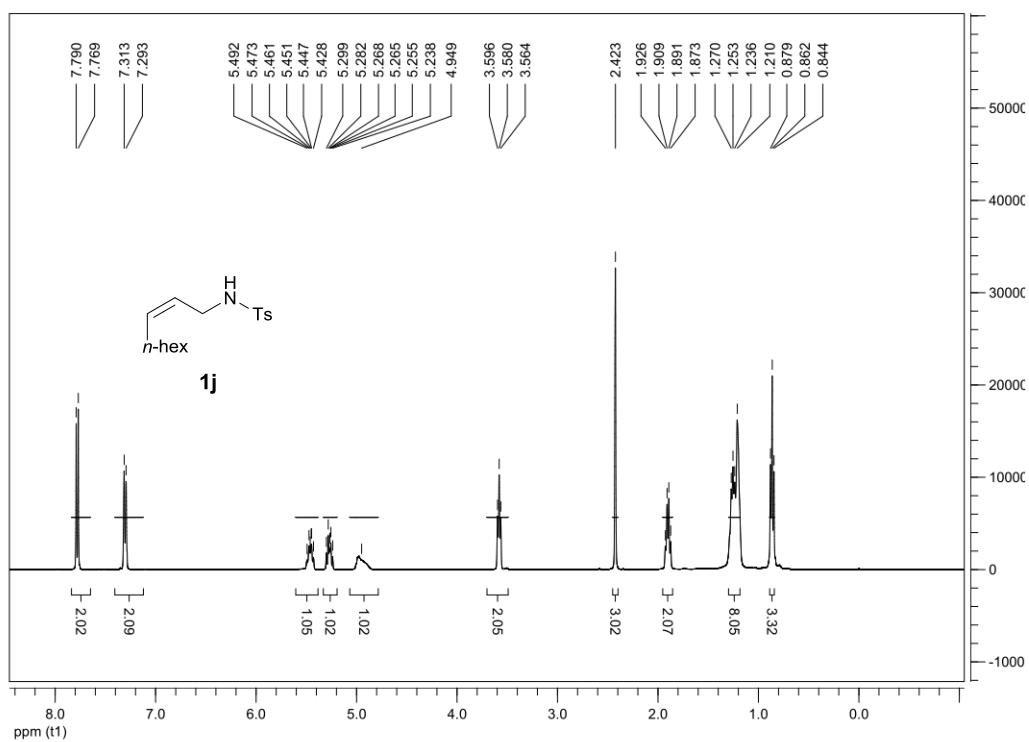
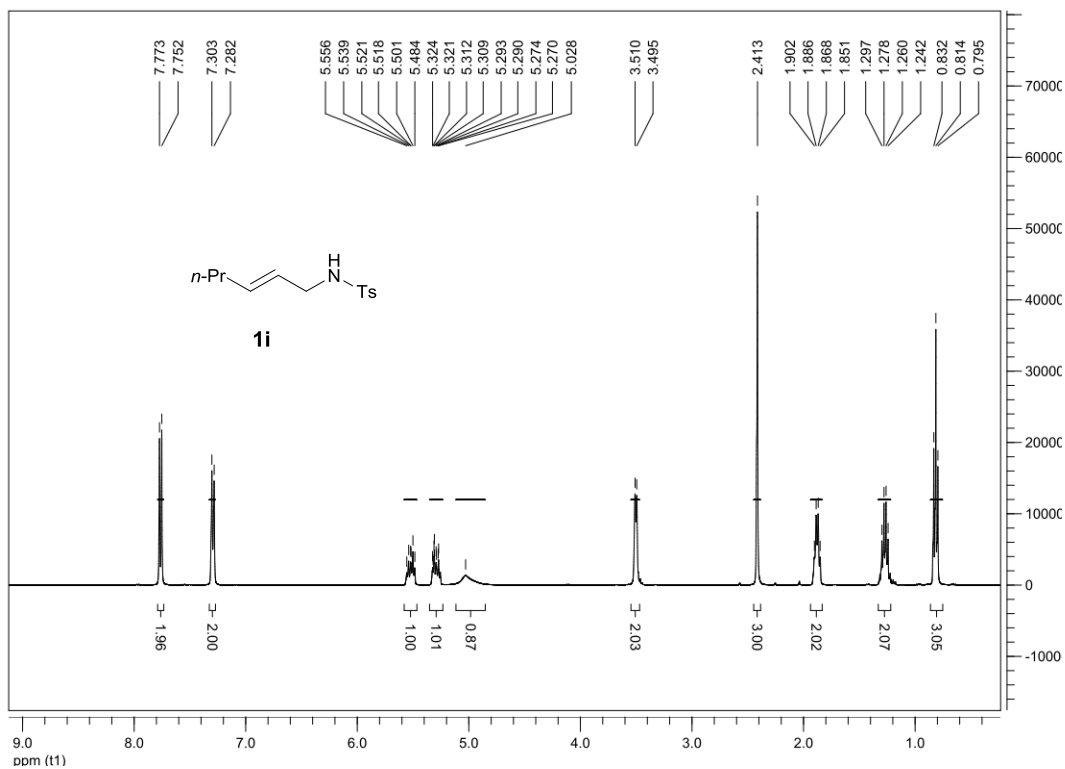
9. Copies of NMR Spectra

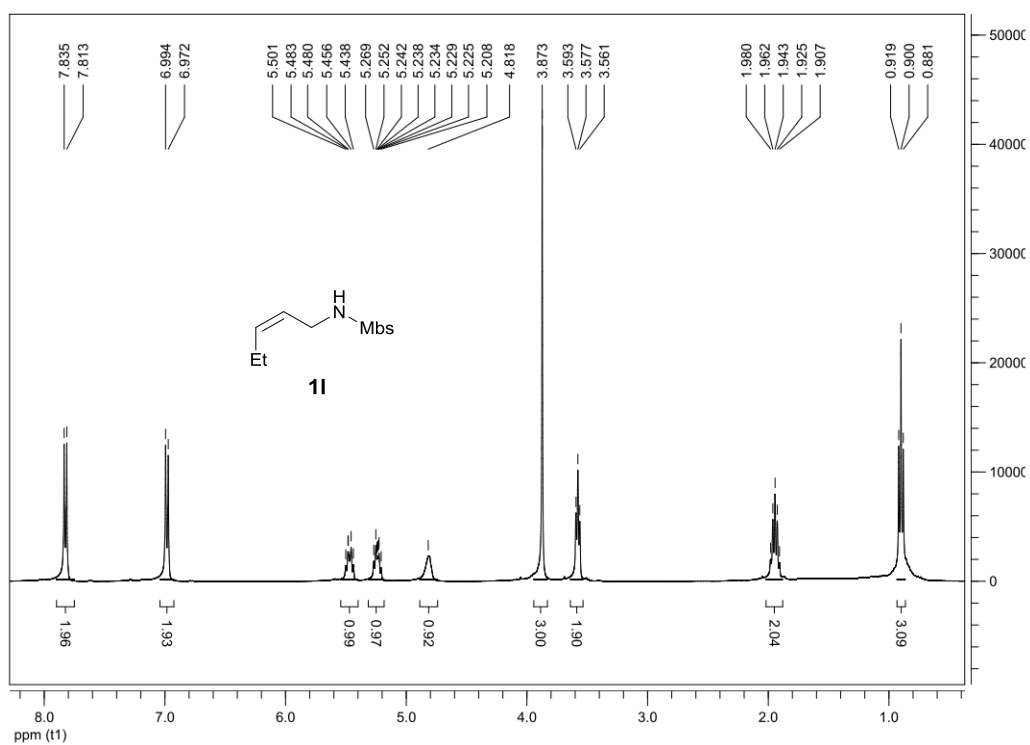
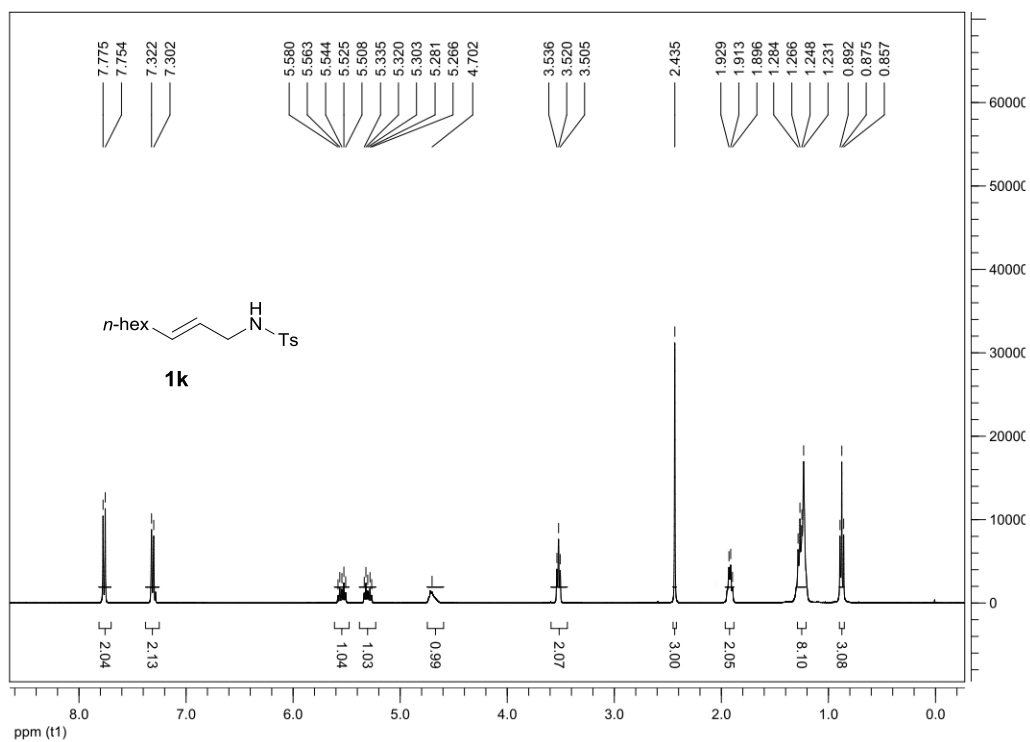


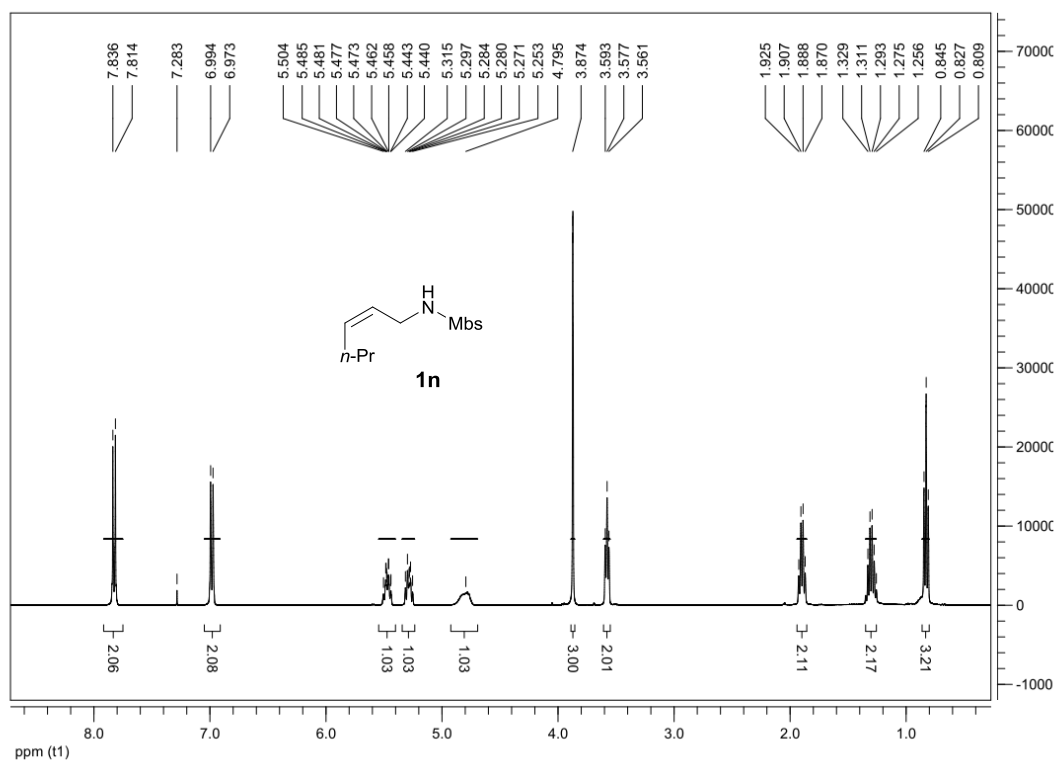
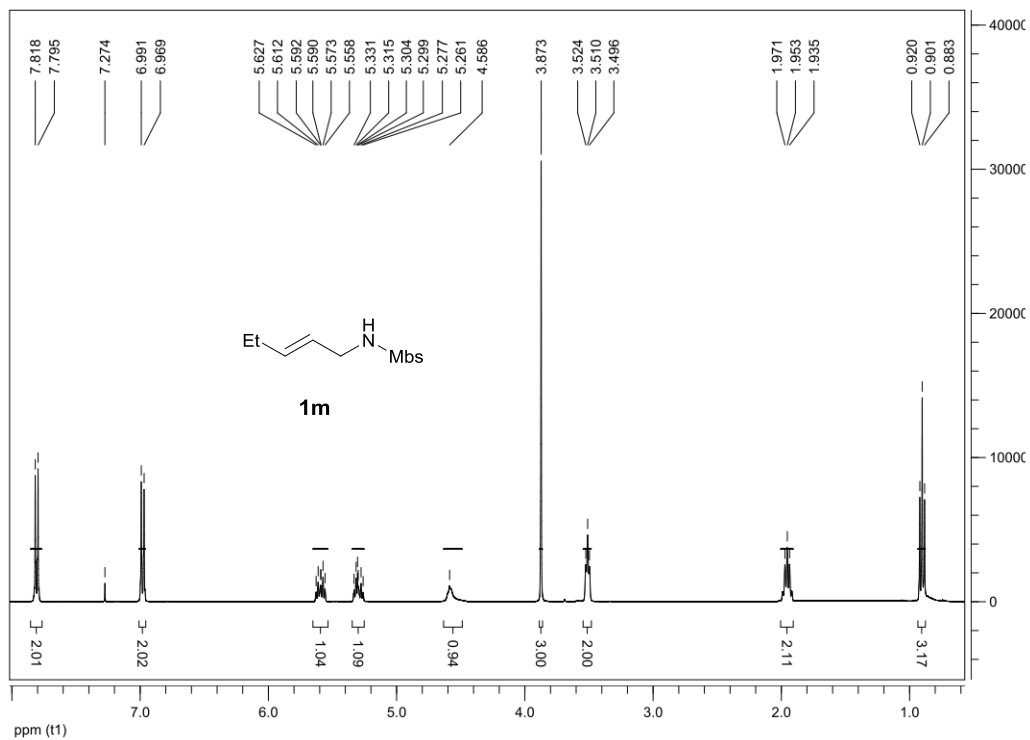


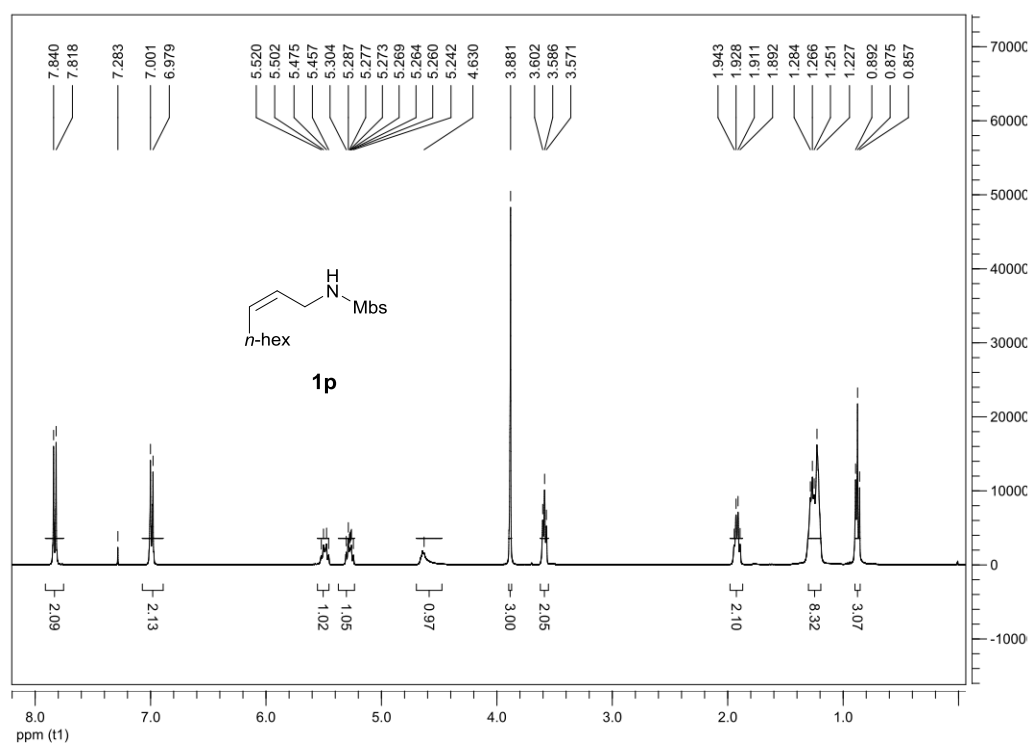
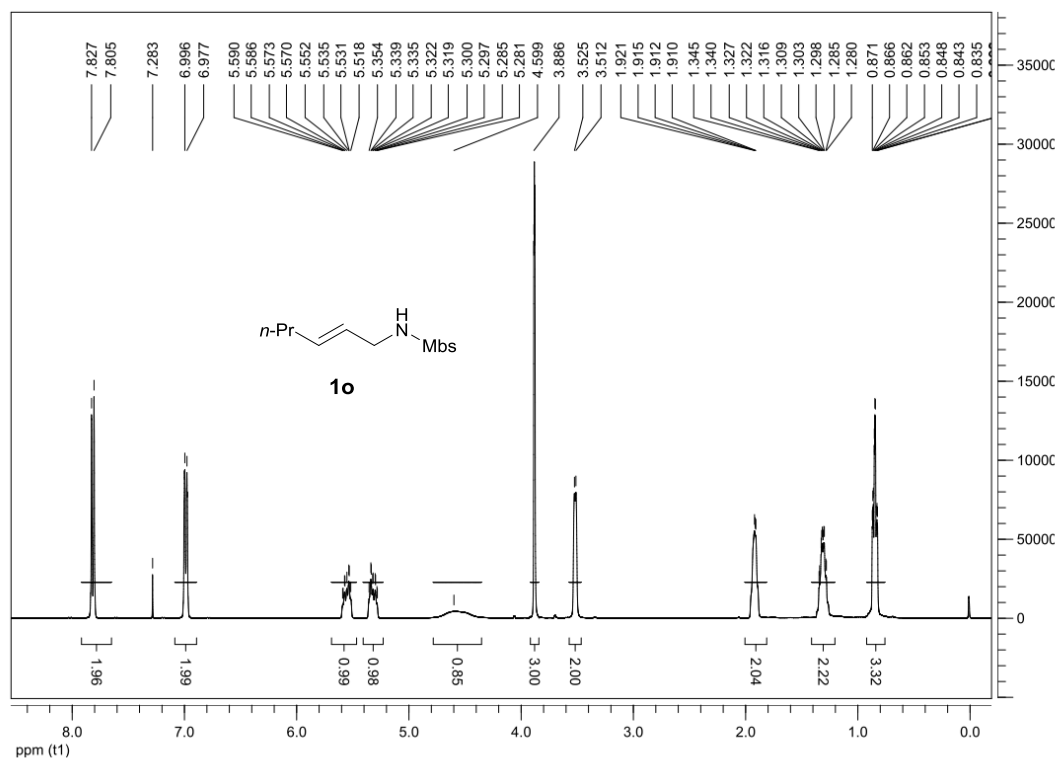


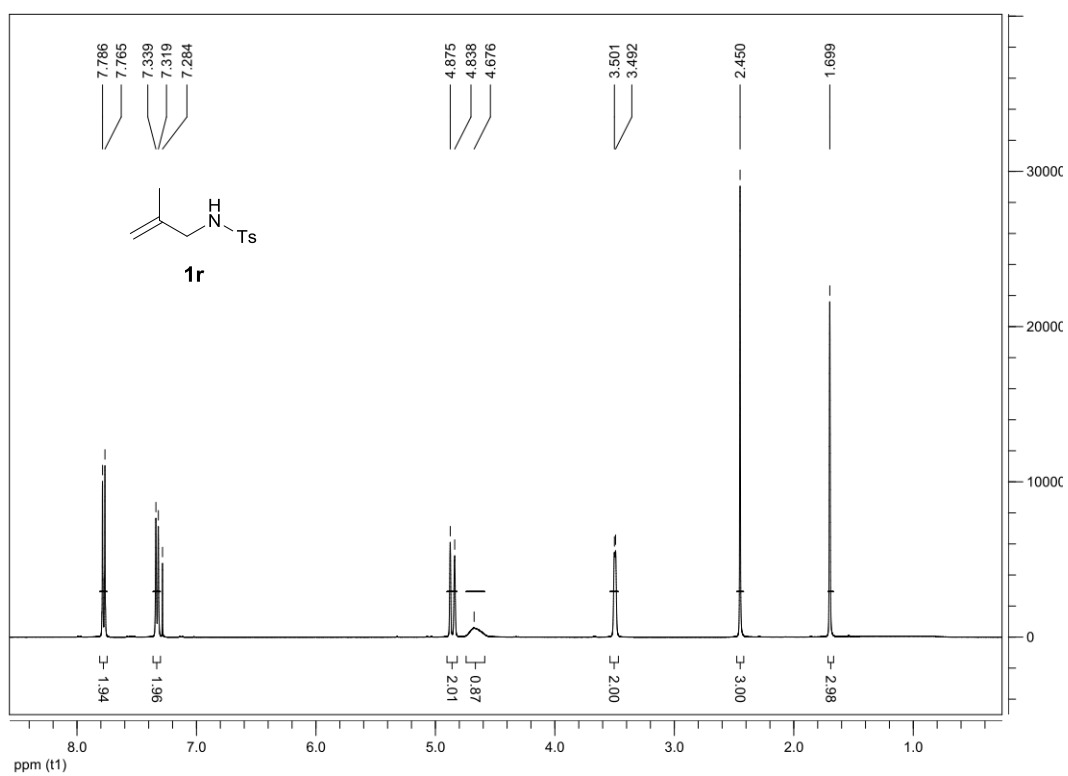
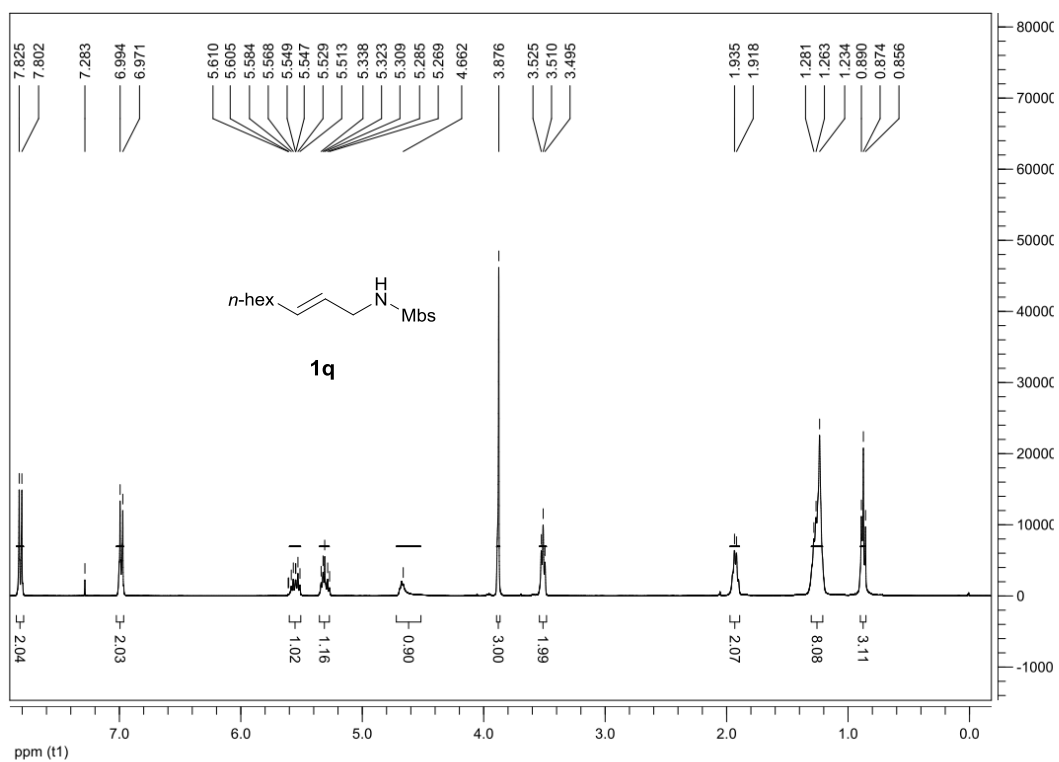


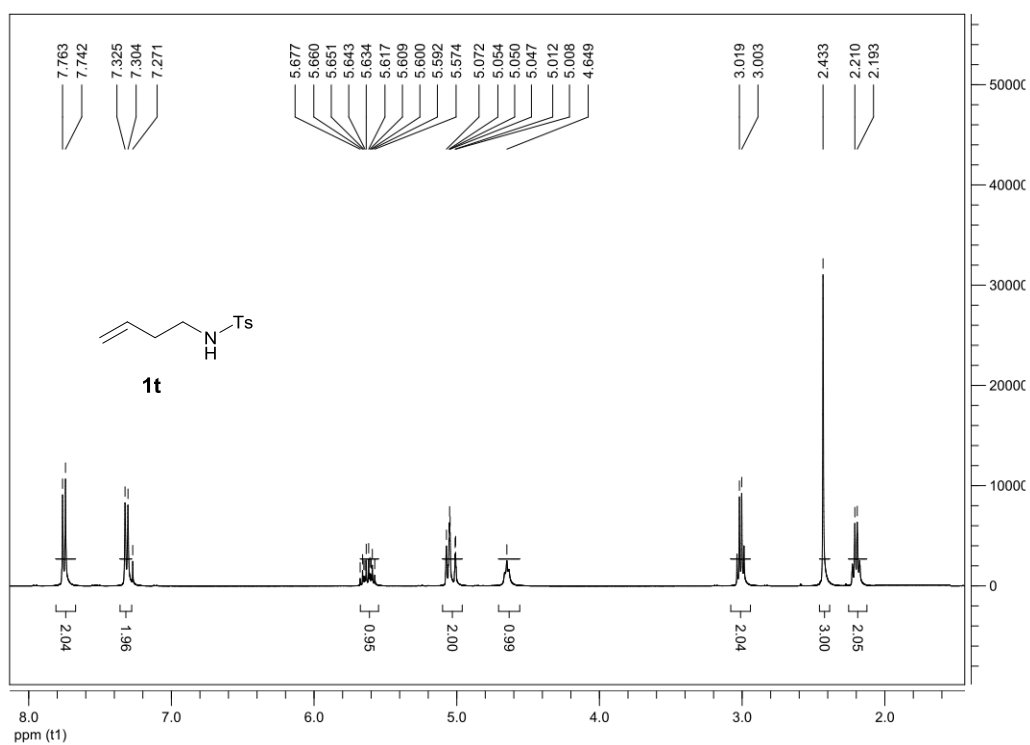
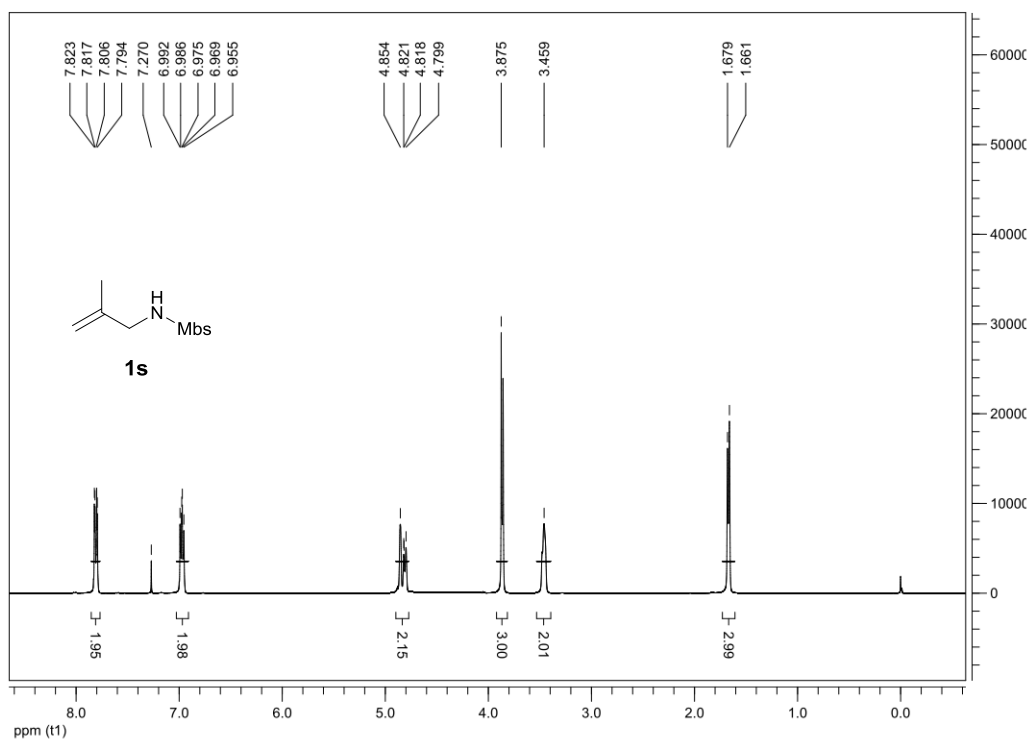


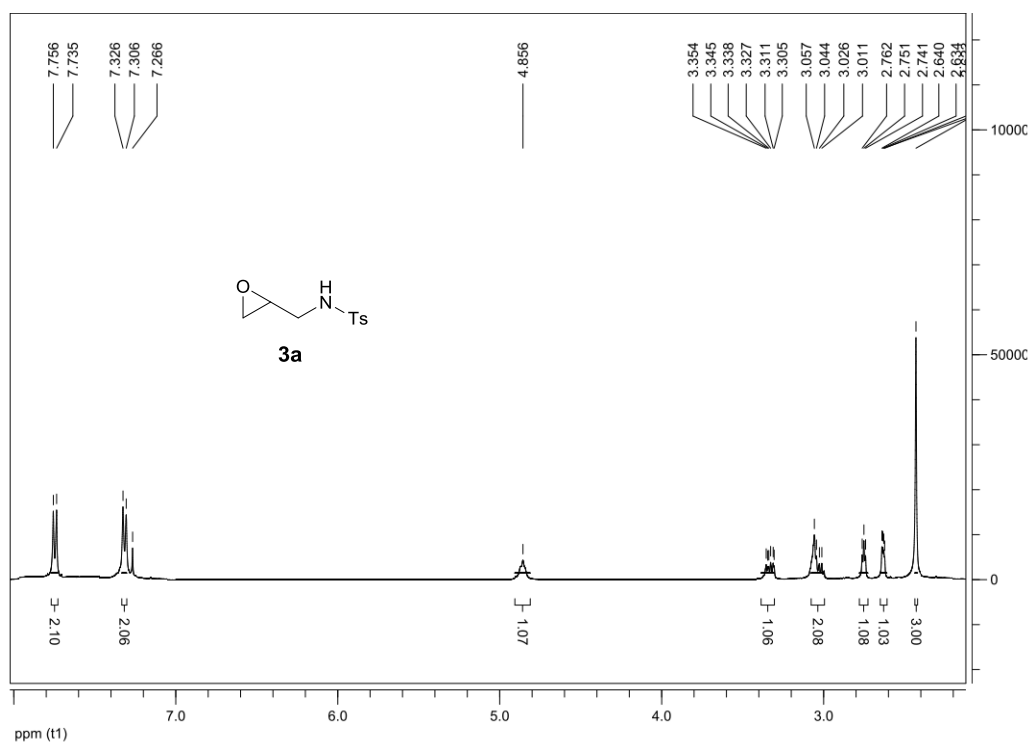
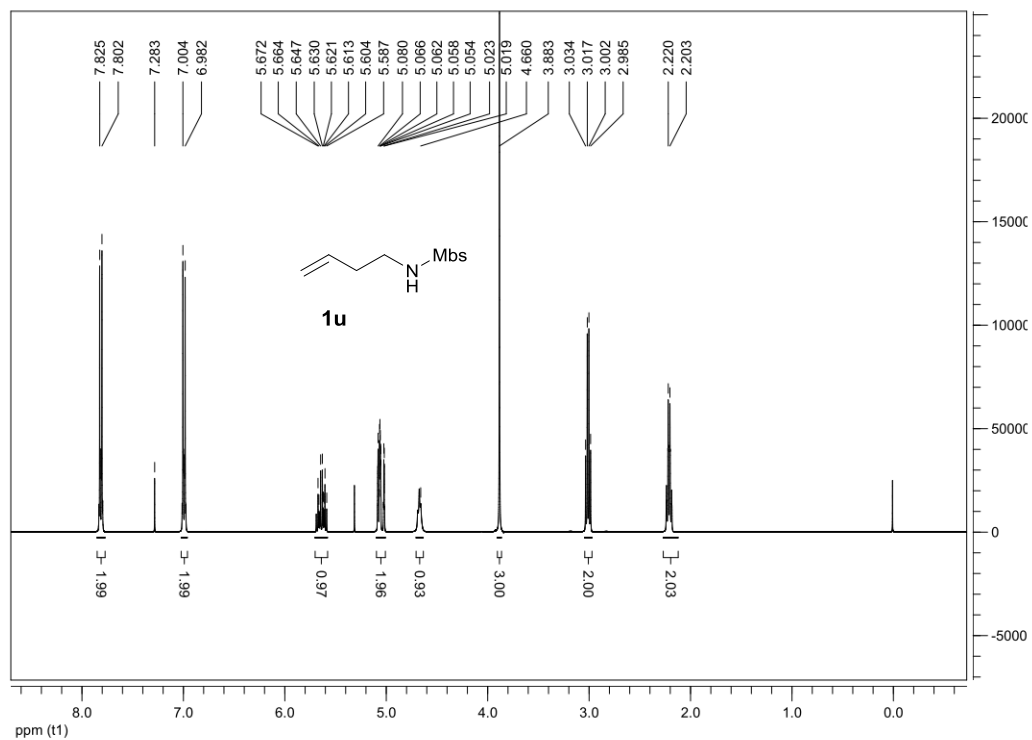


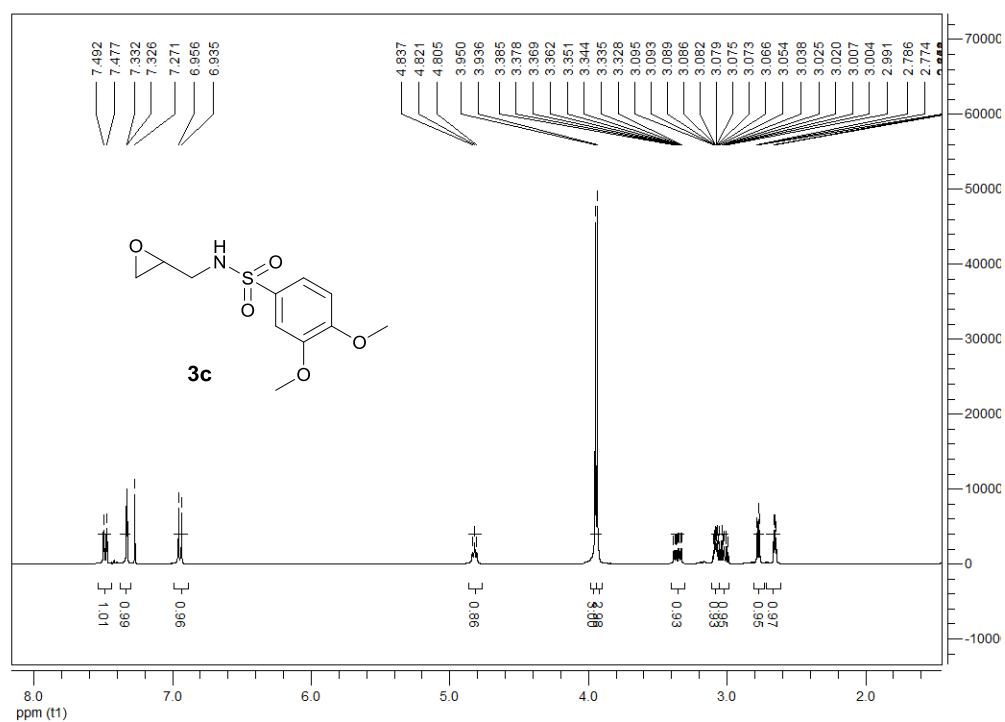
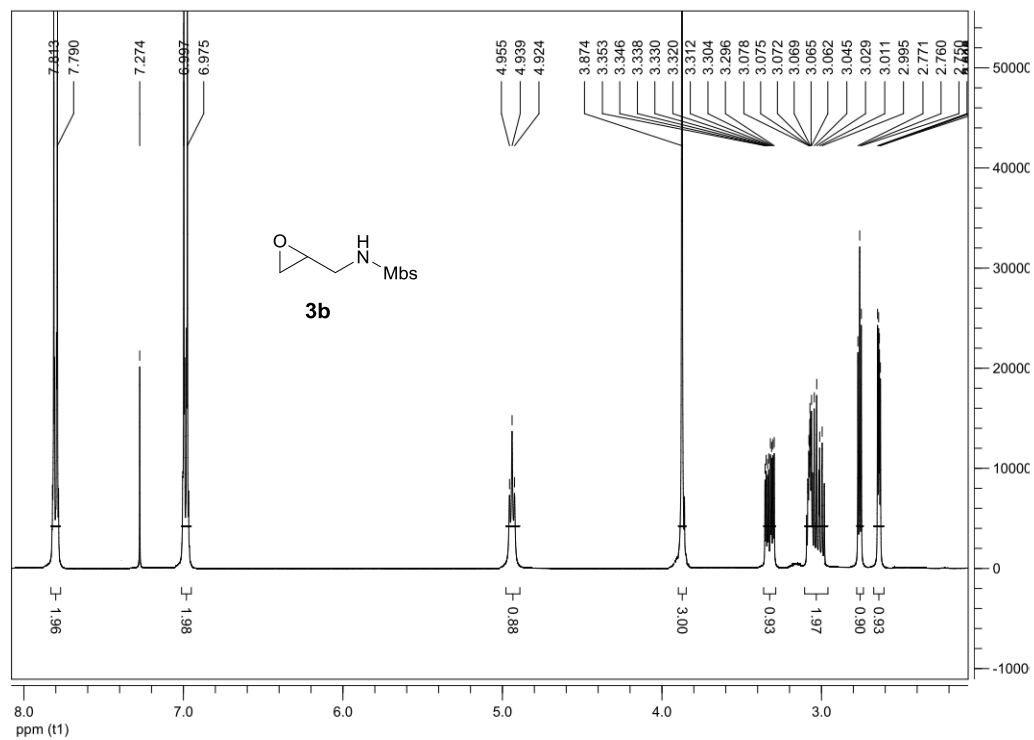


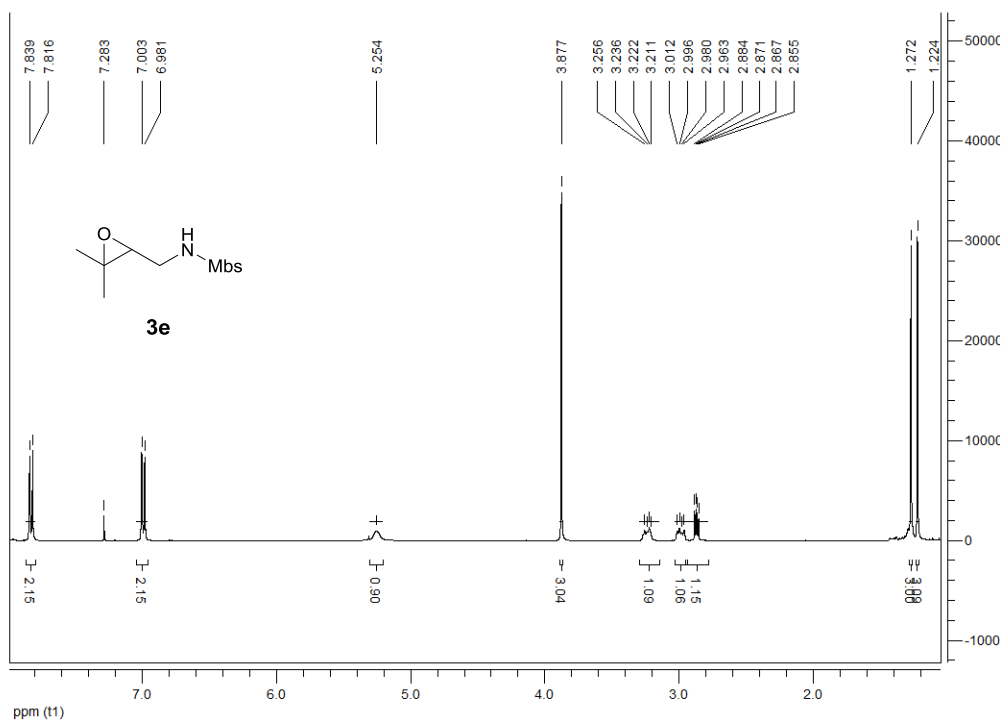
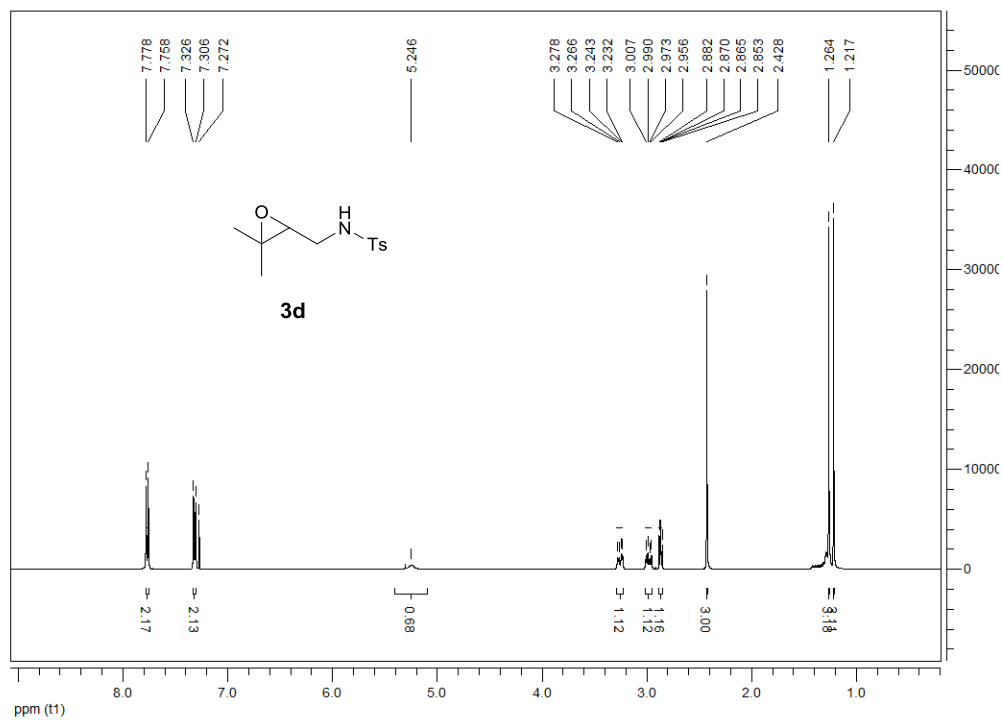


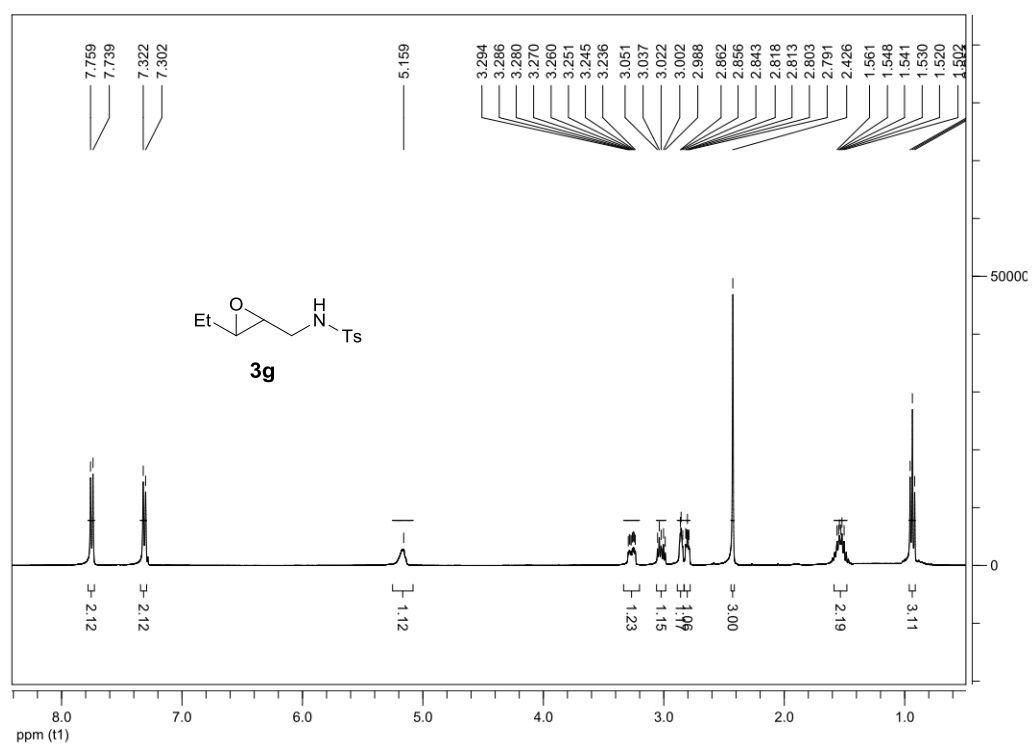
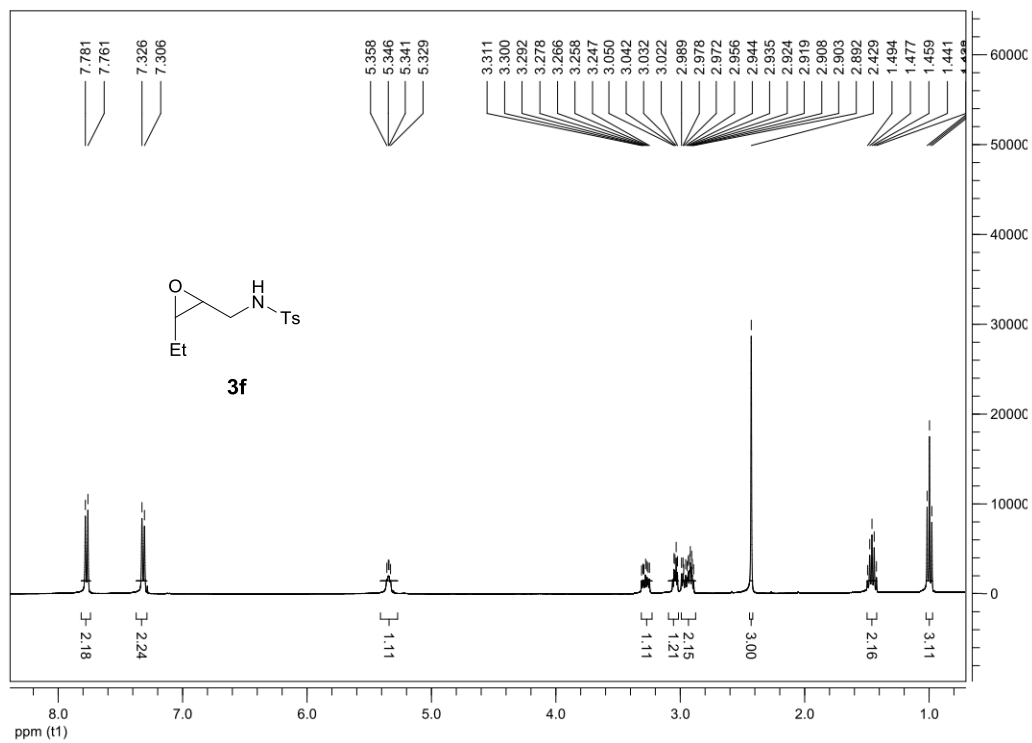


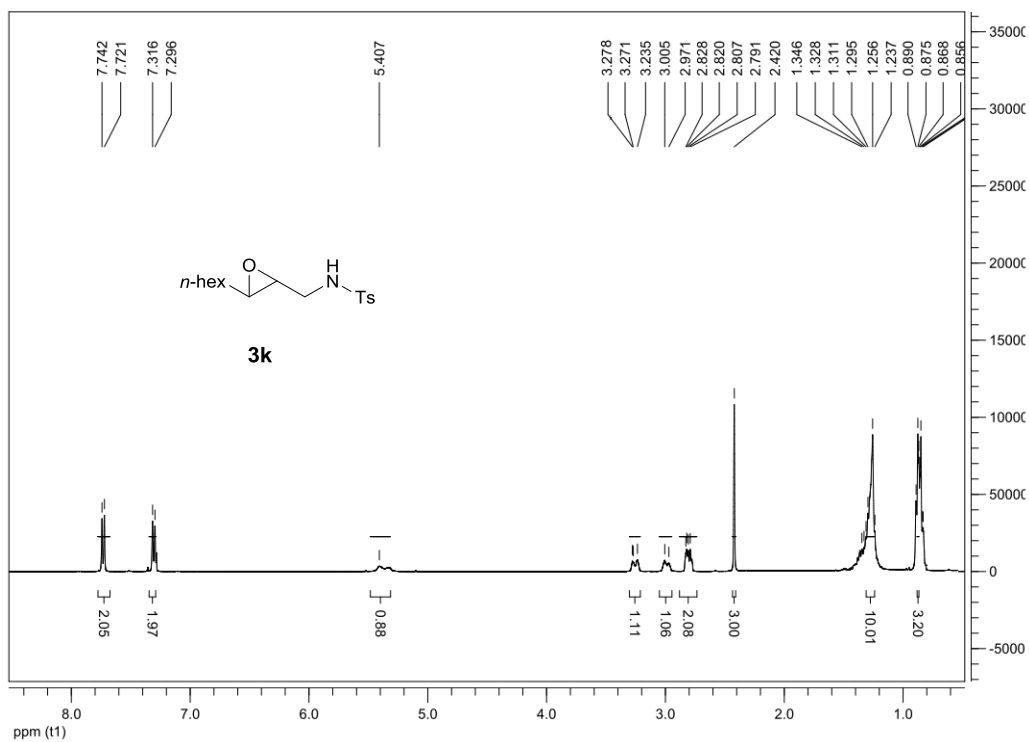
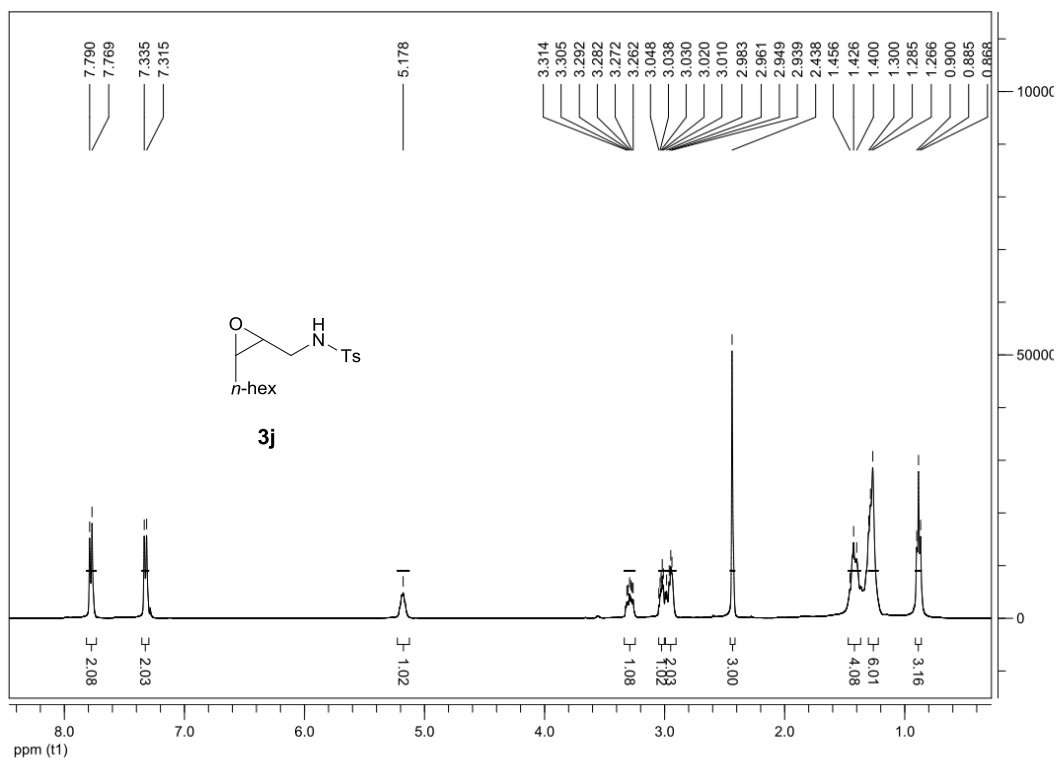


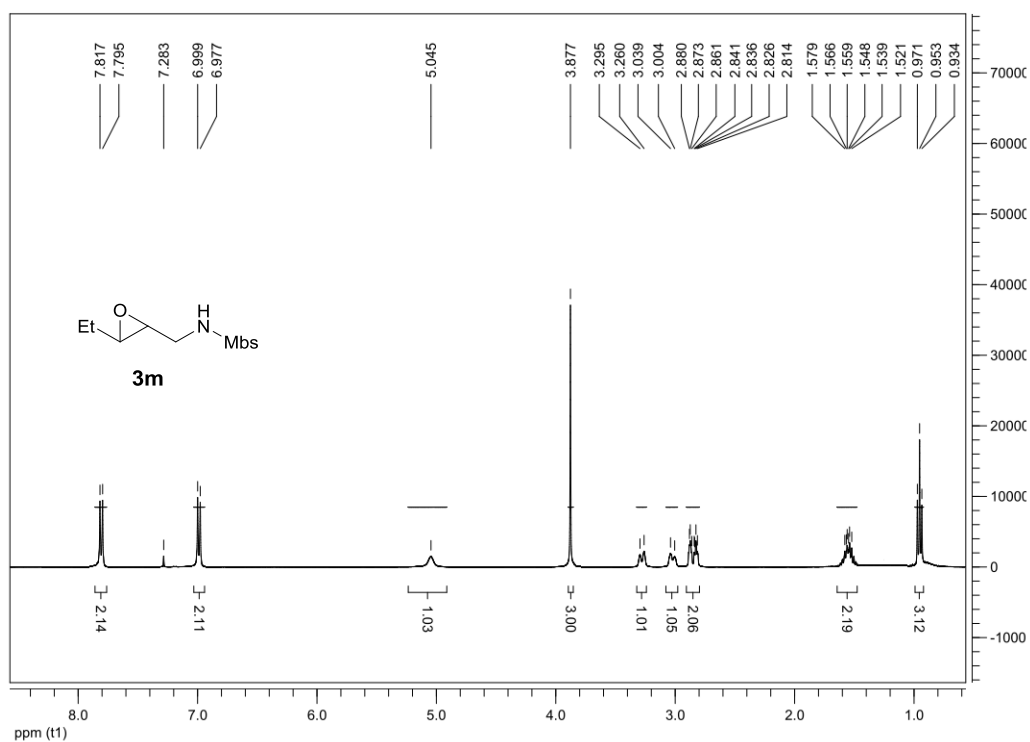
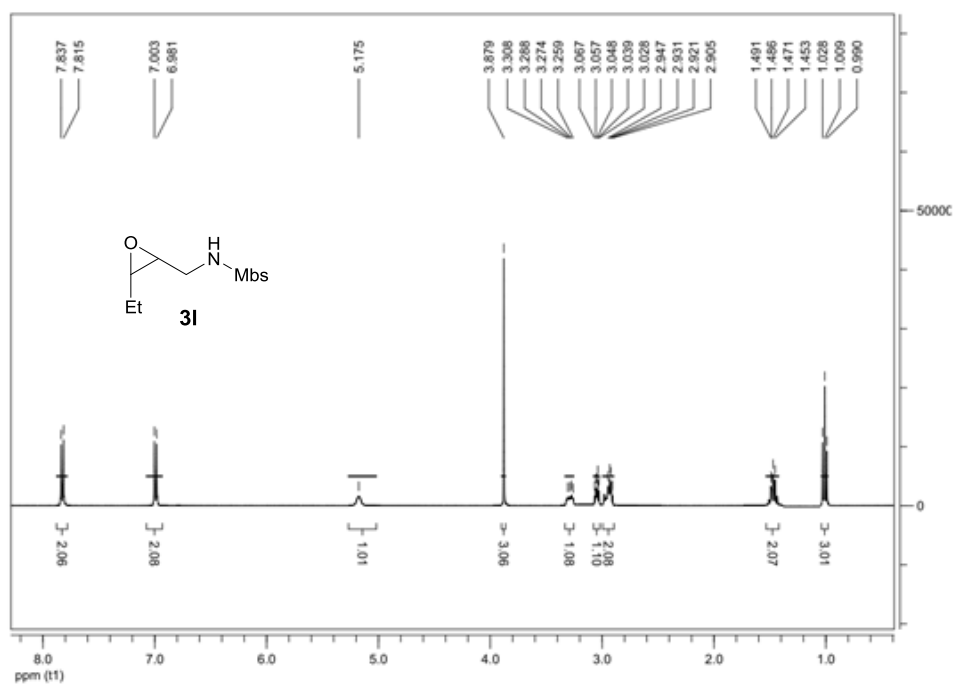


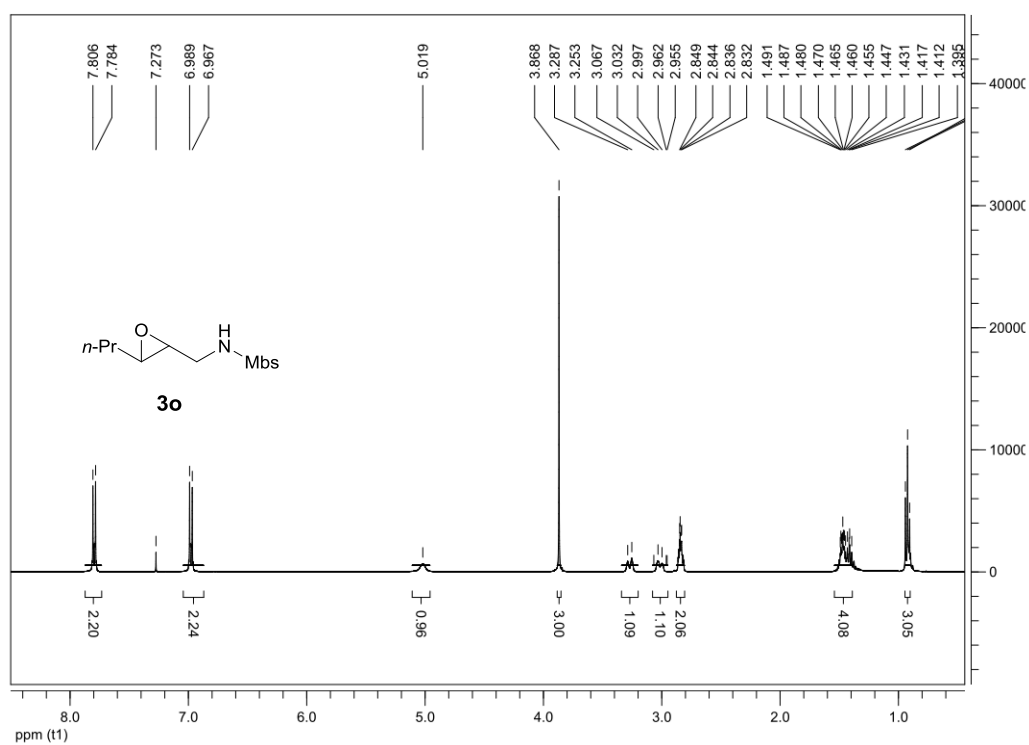
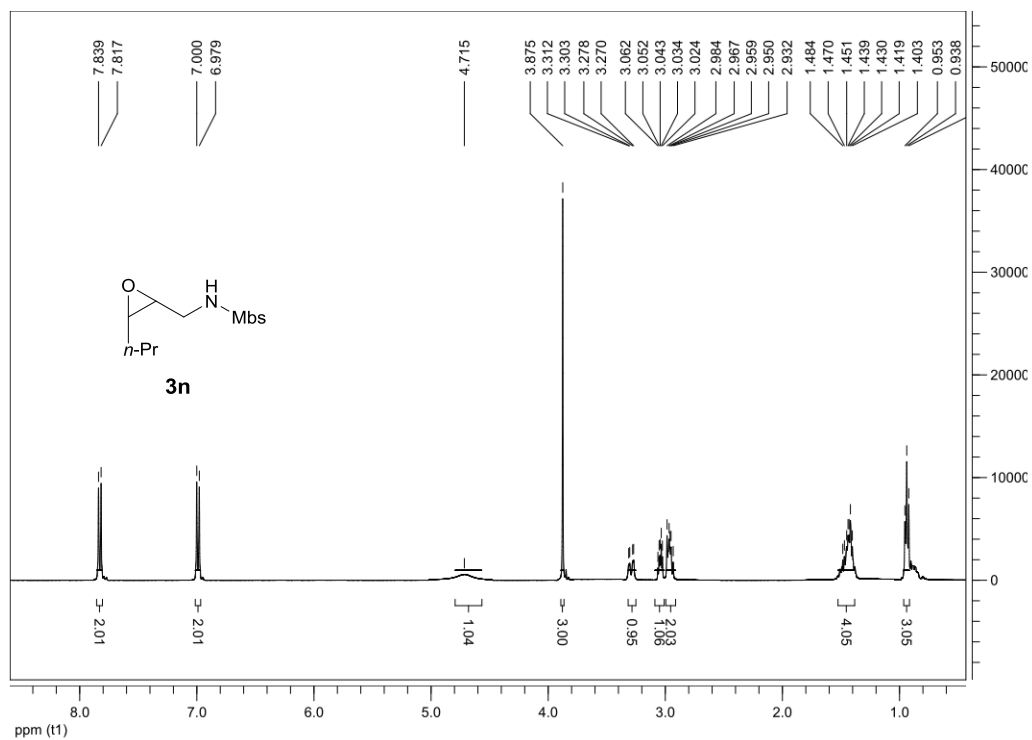


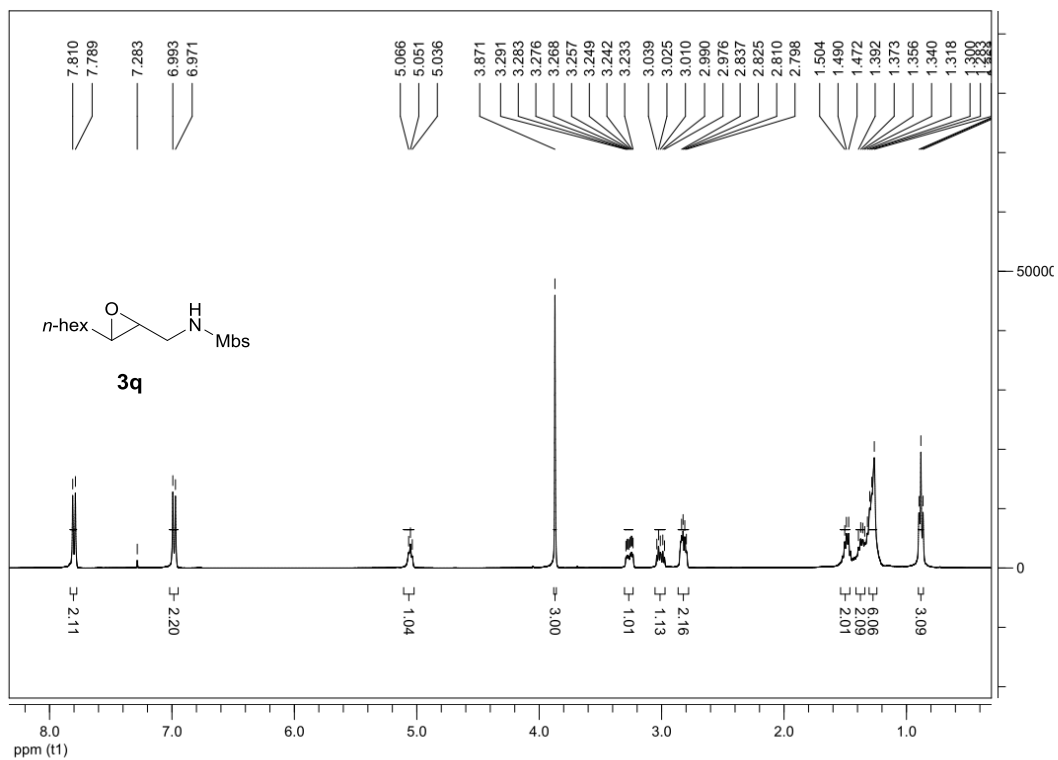
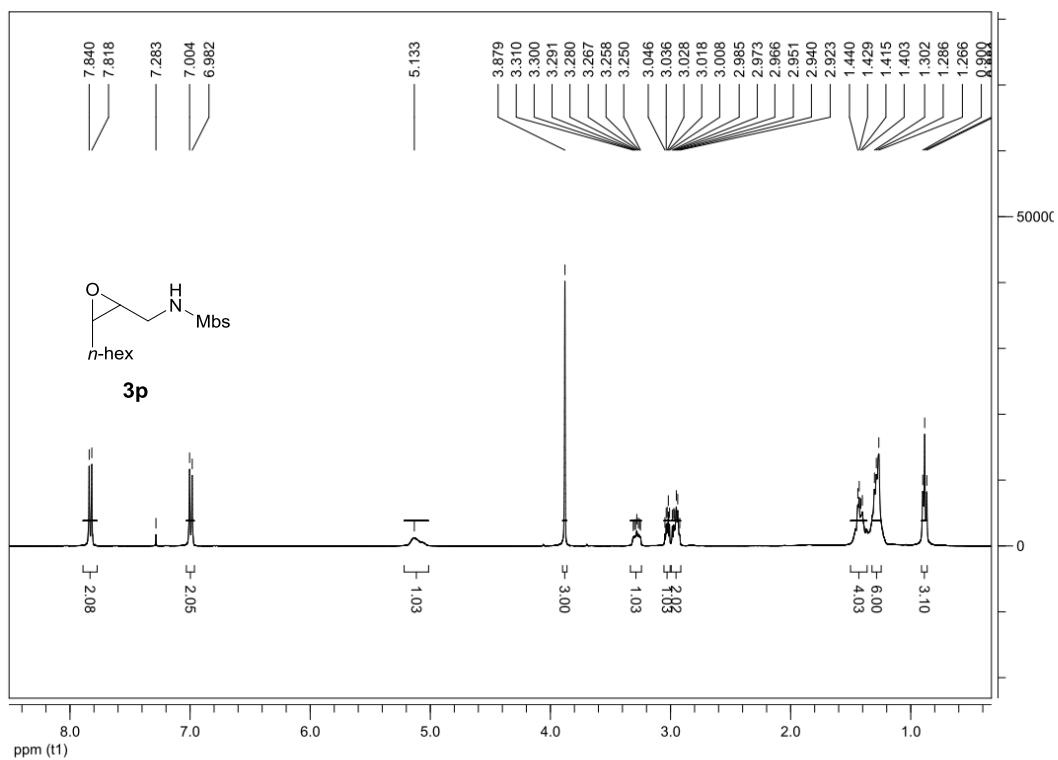


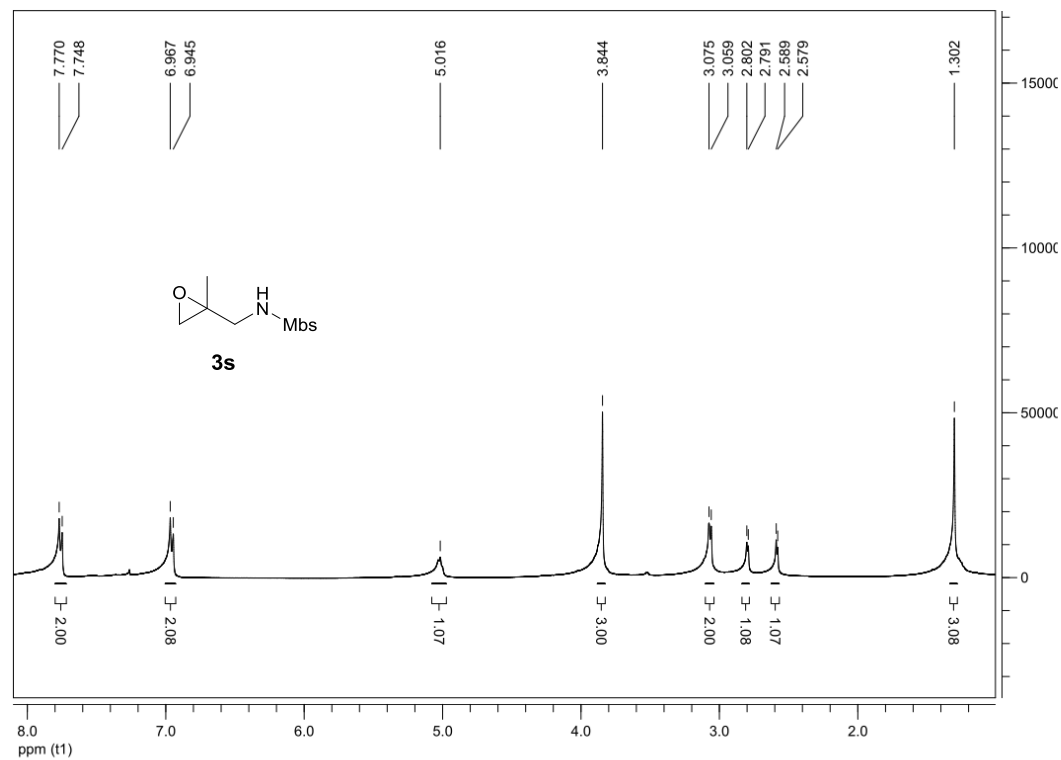
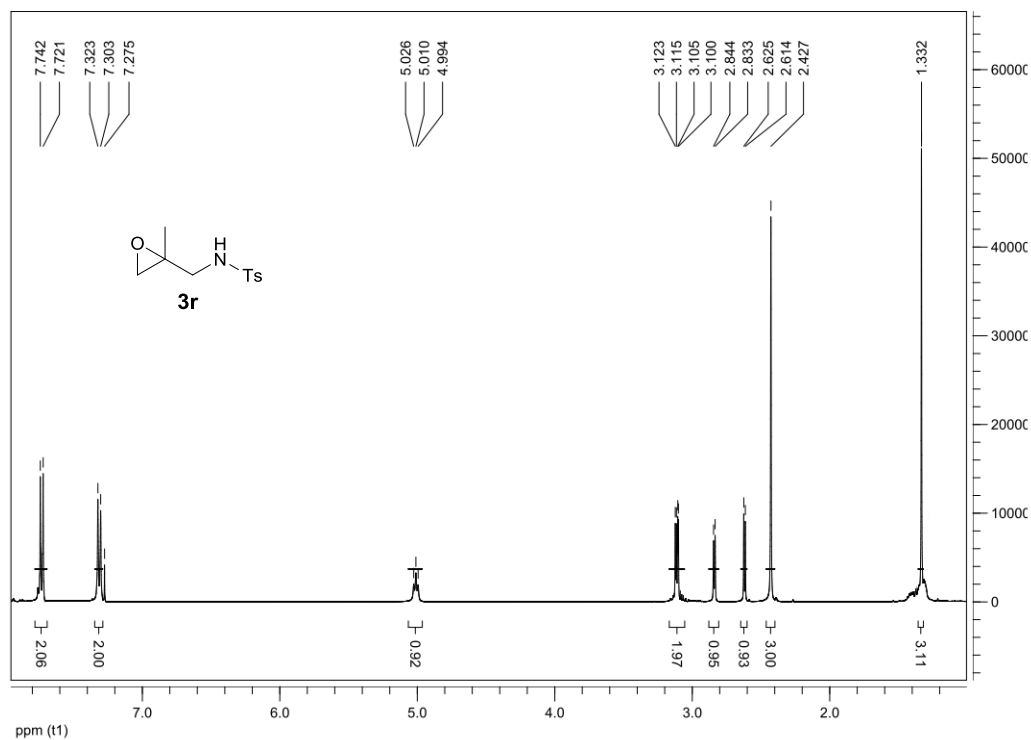


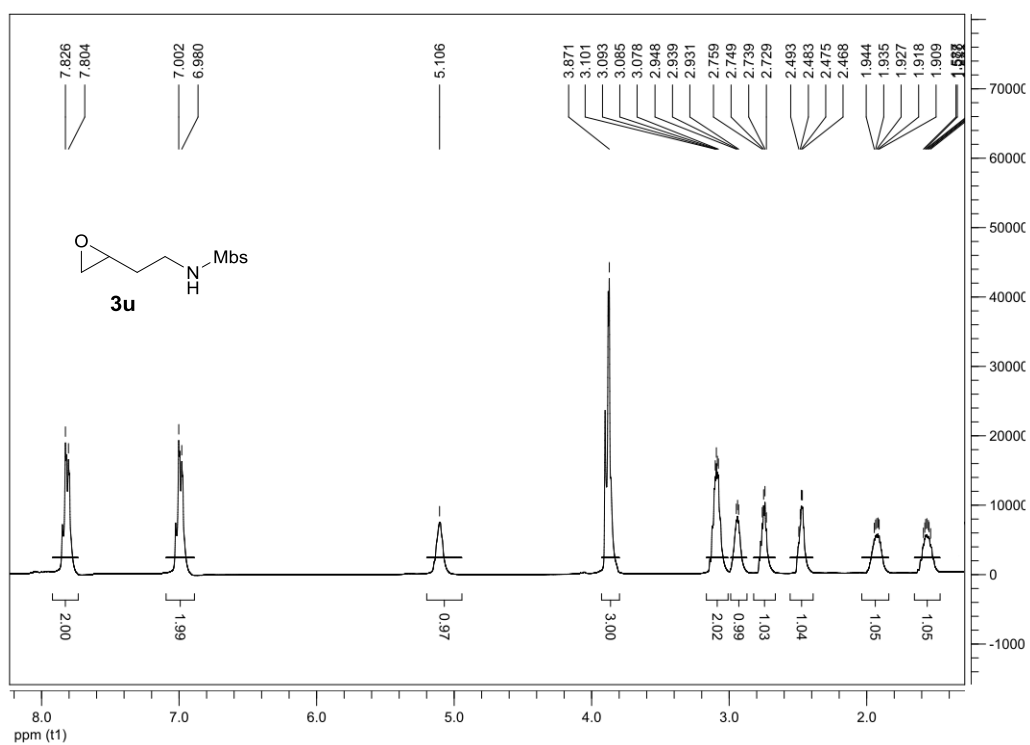
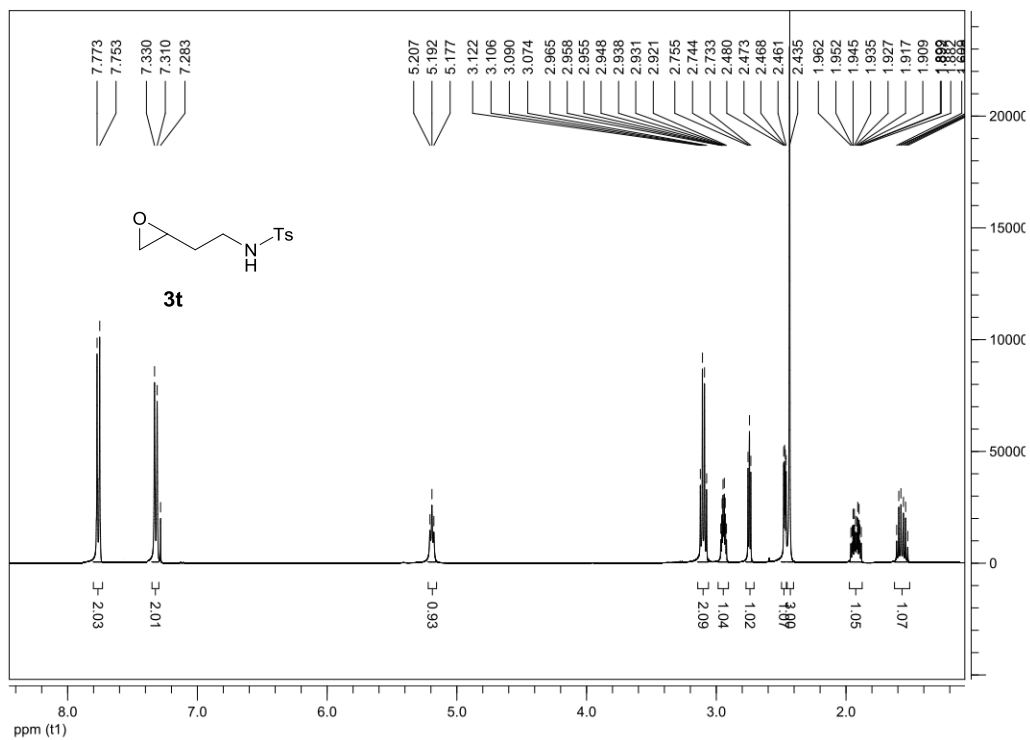


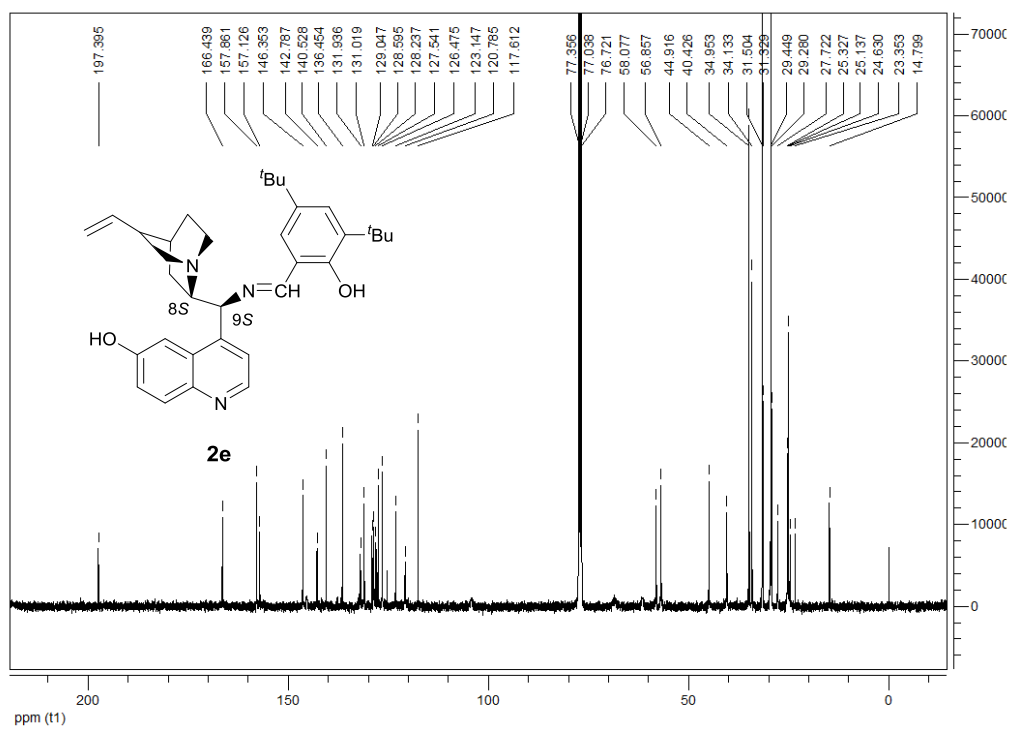
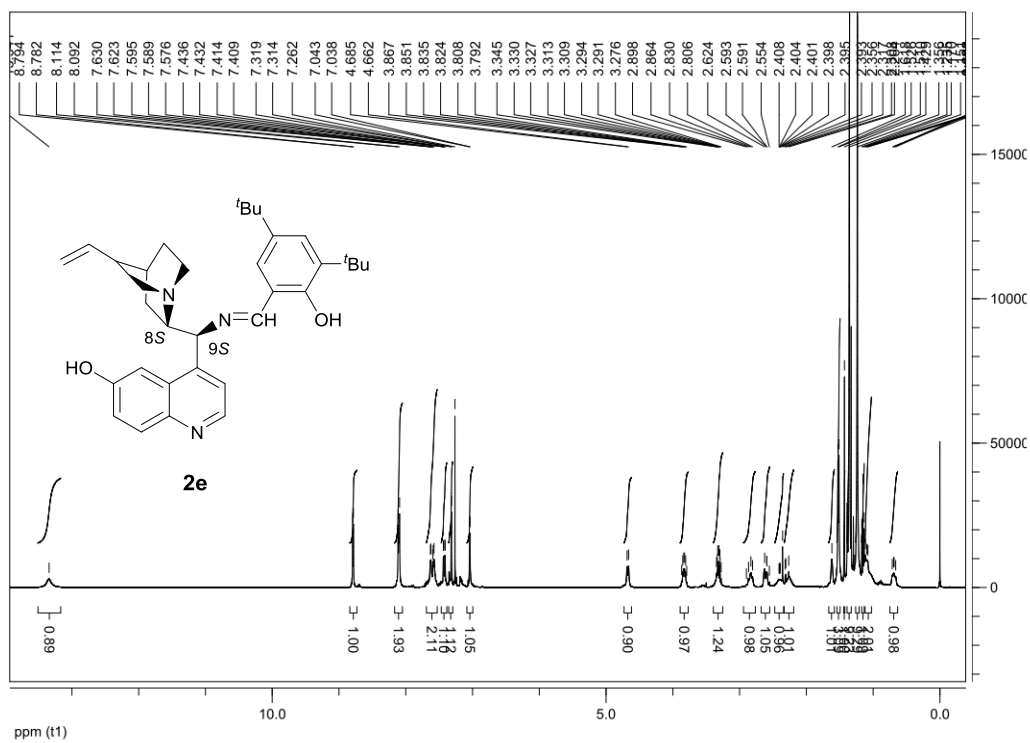


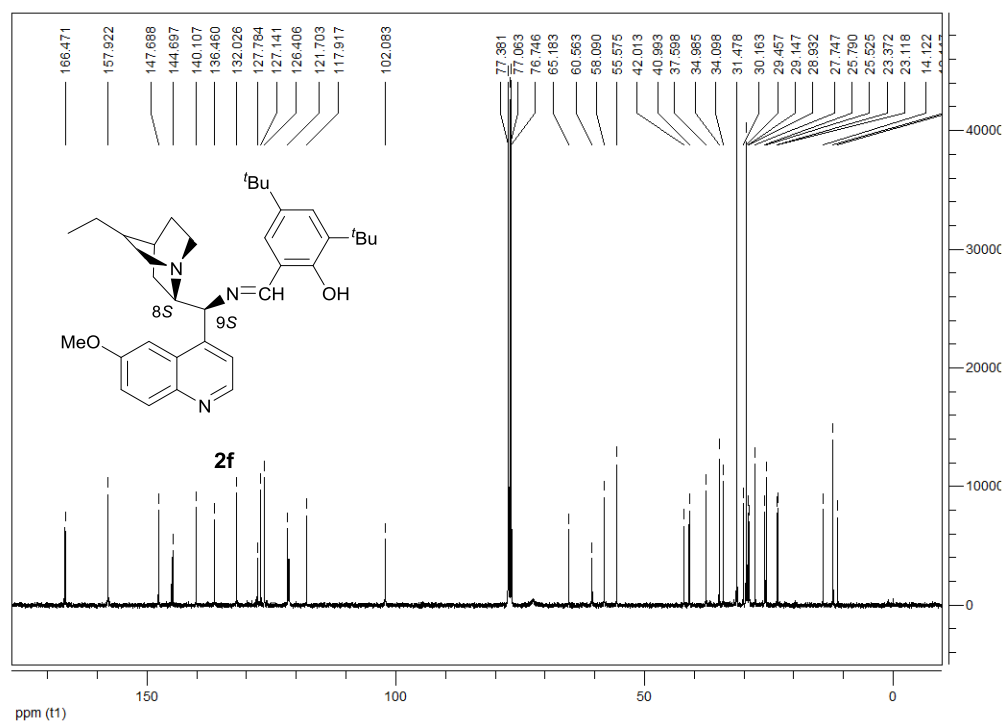
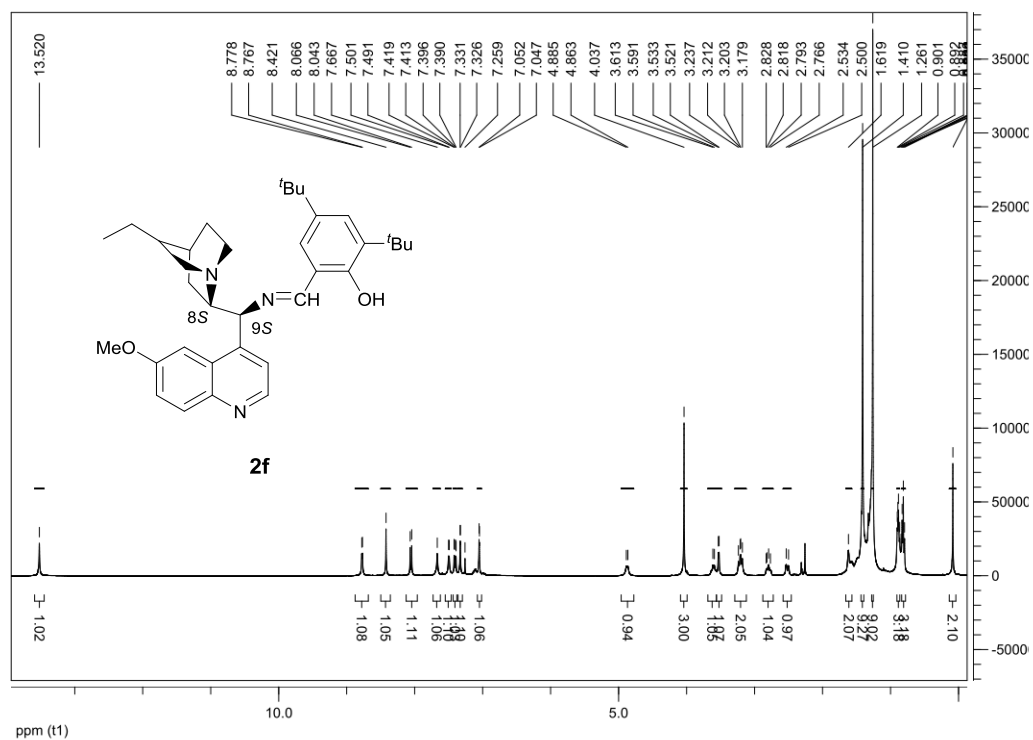




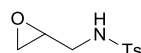




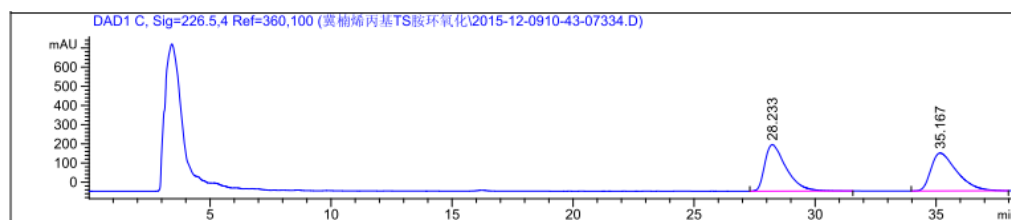




10. Copies of HPLC Analysis



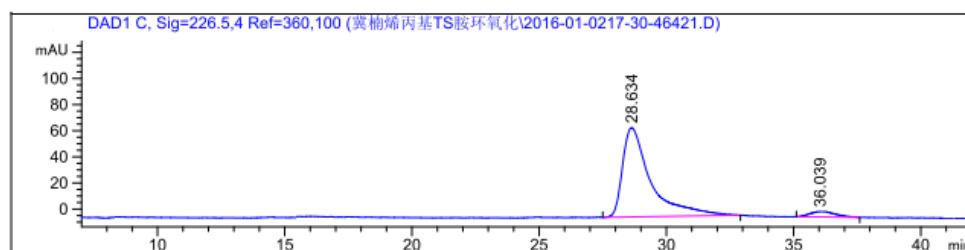
3a: HPLC: Chiralcel OD column, Hx/*i*-PrOH 90:10, 1.0 mL/min. t_{major} : 28.6 min;
 t_{minor} : 36.0 min. (91% ee)



信号 3: DAD1 C, Sig=226.5,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	28.233	BB	0.9163	1.48237e4	242.80467	50.2316
2	35.167	BB	1.1023	1.46870e4	197.79970	49.7684

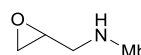
总量 : 2.95106e4 440.60437



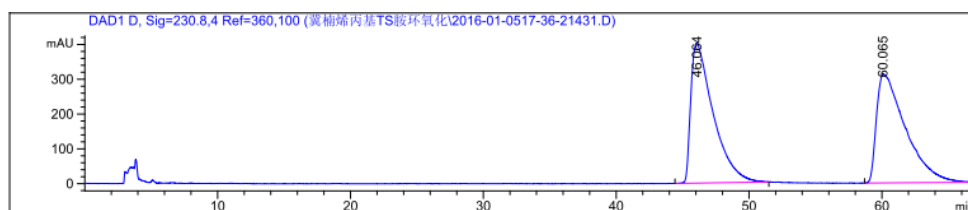
信号 3: DAD1 C, Sig=226.5,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	28.634	BB	1.0988	5249.21924	68.28967	95.6114
2	36.039	MM	1.0577	240.93842	3.79644	4.3886

总量 : 5490.15765 72.08610



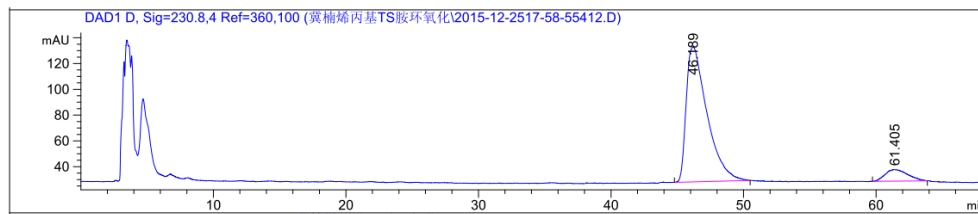
3b: HPLC: Chiralcel OD column, Hx/*i*-PrOH 90:10, 1.0 mL/min. t_{major} : 46.1 min;
 t_{minor} : 61.4 min. (85% ee)



信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	46.064	BB	1.5786	4.70135e4	403.11078	49.8535
2	60.065	BBA	1.9537	4.72897e4	314.24783	50.1465

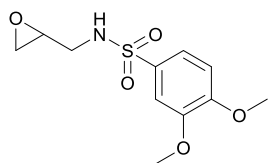
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信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

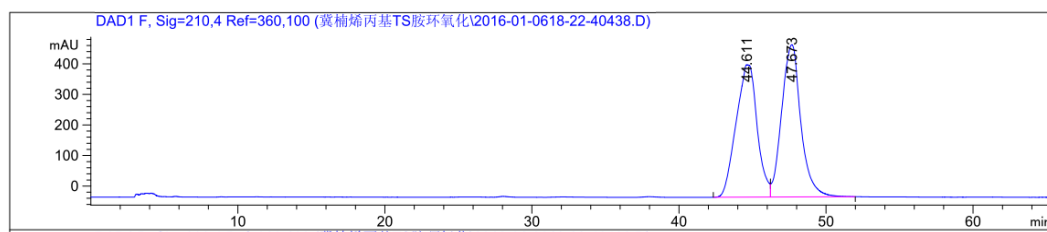
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	46.189	BB	1.5343	1.14098e4	104.62241	92.2497
2	61.405	MM	1.8681	958.59442	8.55253	7.7503

总量 : 1.23684e4 113.17493



3c: HPLC: Chiralcel AD column, Hx/*i*-PrOH 90:10, 1.0 mL/min. t_{minor} :

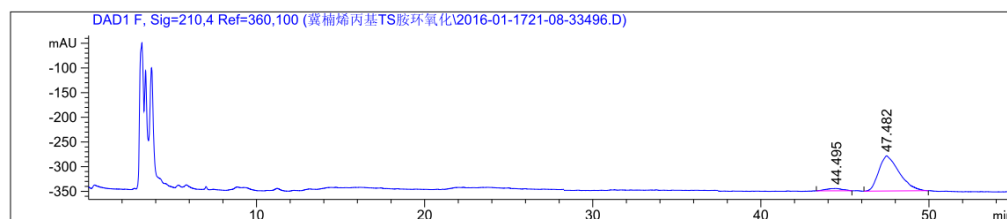
44.4 min; t_{major} : 47.4 min. (91% ee)



信号 6: DAD1 F, Sig=210,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	44.611	BV	1.2158	4.30001e4	433.30856	48.7538
2	47.673	VB	1.2404	4.51983e4	498.19653	51.2462

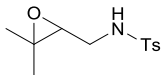
总量 : 8.81984e4 931.50510



信号 6: DAD1 F, Sig=210,4 Ref=360,100

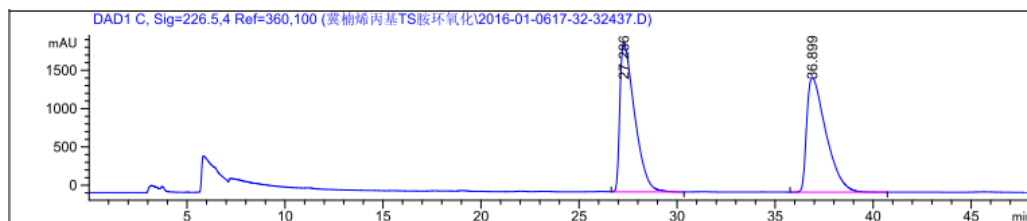
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	44.495	MM	1.1198	296.13376	4.40749	4.7150
2	47.482	BB	1.0352	5984.52246	71.30537	95.2850

总量 : 6280.65622 75.71286



3d: HPLC: Chiralcel AD column, Hx/*i*-PrOH 90:10, 1.0 mL/min. t_{minor} : 28.1 min;

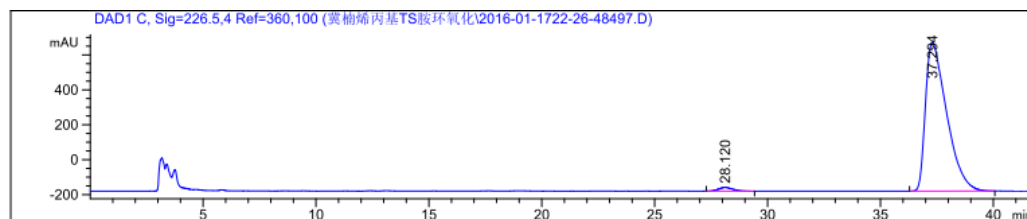
t_{major} : 37.2 min. (97% ee)



信号 3: DAD1 C, Sig=226.5,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	27.286	VB	0.7491	1.01621e5	1946.59961	49.9053
2	36.899	BB	1.0108	1.02007e5	1497.26746	50.0947

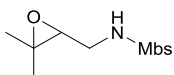
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信号 3: DAD1 C, Sig=226.5,4 Ref=360,100

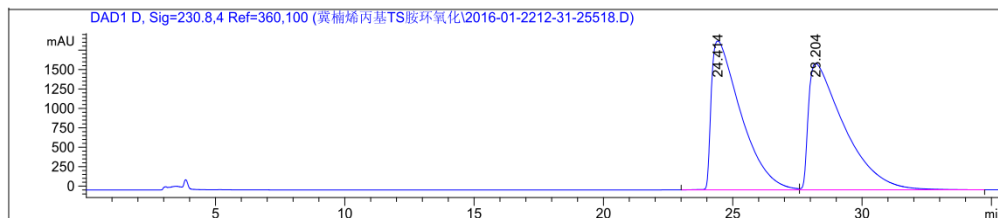
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	28.120	BB	0.6271	913.81750	21.19308	1.6259
2	37.294	BB	0.9904	5.52902e4	852.84375	98.3741

总量 : 5.62041e4 874.03683



3e: HPLC: Chiralcel OD column, Hx/*i*-PrOH 90:10, 1.0 mL/min. t_{major} : 24.8 min;

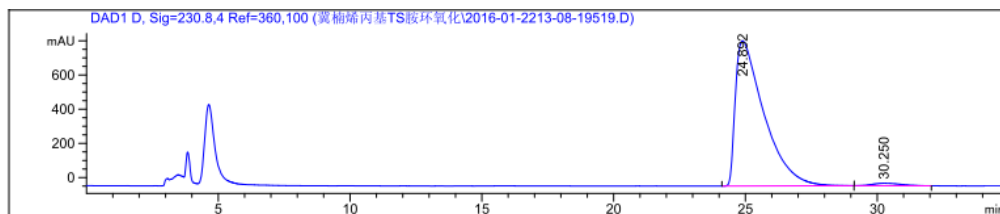
t_{minor} : 30.2 min. (97% ee)



信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	24.414	BV	1.0418	1.52009e5	1915.53308	49.2374
2	29.204	VB	1.2779	1.56718e5	1623.97070	50.7626

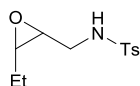
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信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

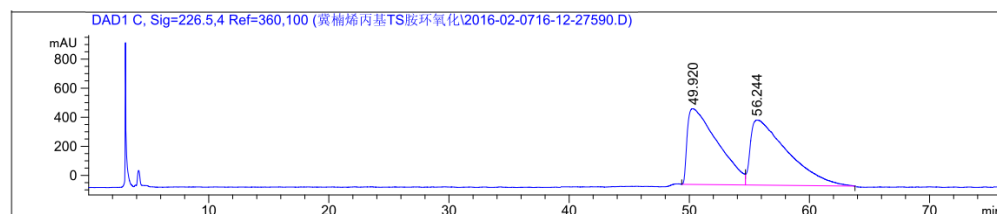
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	24.892	BB	1.0903	6.39524e4	849.46735	98.3614
2	30.250	BB	0.8840	1065.37988	14.38575	1.6386

总量 : 6.50178e4 863.85309



3f: HPLC: Chiralcel OD column, Hx/i-PrOH 97:3, 1.0 mL/min. t_{major} : 47.3 min;

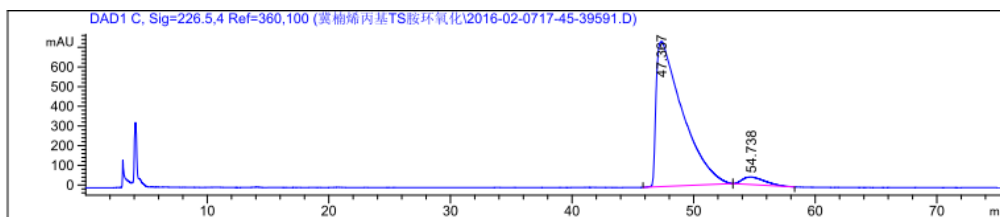
t_{minor} : 54.7 min. (91% ee)



信号 3: DAD1 C, Sig=226.5,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	49.920	BV	2.0613	9.13828e4	520.75952	48.6376
2	56.244	VB	2.5235	9.65025e4	447.20691	51.3624

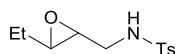
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信号 3: DAD1 C, Sig=226.5,4 Ref=360,100

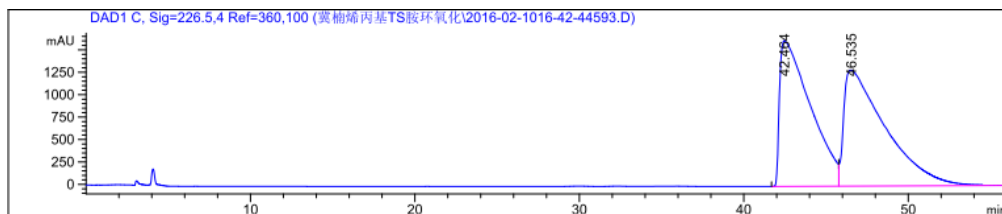
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	47.367	BB	2.0037	1.11055e5	737.11688	95.7546
2	54.738	BB	1.5314	4923.79443	38.77654	4.2454

总量 : 1.15979e5 775.89342



3g: HPLC: Chiralcel OD column, Hx/i-PrOH 97:3, 1.0 mL/min. t_{major} : 44.4 min;

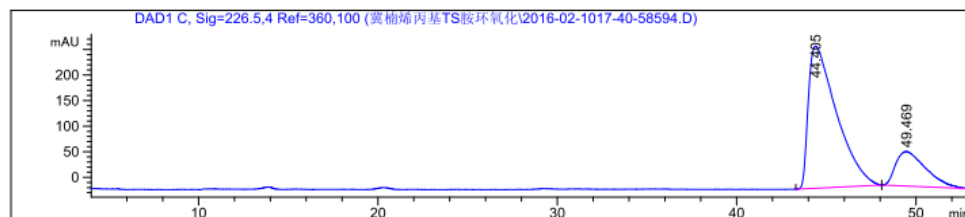
t_{minor} : 49.4 min. (63% ee)



信号 3: DAD1 C, Sig=226.5,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	42.464	BV	1.6380	2.10976e5	1627.92798	48.0414
2	46.535	VBA	2.0742	2.28179e5	1292.12549	51.9586

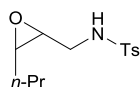
总量 : 4.39155e5 2920.05347



信号 3: DAD1 C, Sig=226.5,4 Ref=360,100

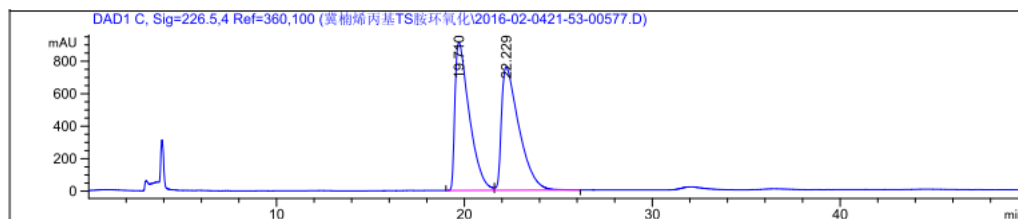
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	44.405	BB	1.5600	1.59910e4	277.68640	81.1674
2	49.469	BBA	1.4298	3710.25439	67.51863	18.8326

总量 : 1.97013e4 345.20503



3h: HPLC: Chiralcel OD column, Hx/*i*-PrOH 92:8, 1.0 mL/min. t_{major} : 19.6 min;

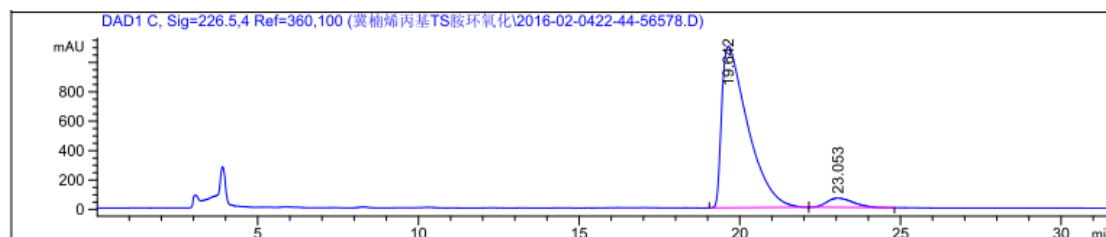
t_{minor} : 23.0 min. (91% ee)



信号 3: DAD1 C, Sig=226.5,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.710	BV	0.7824	4.83101e4	911.41846	49.6038
2	22.229	VB	0.9546	4.90818e4	758.86005	50.3962

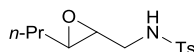
总量 : 9.73919e4 1670.27850



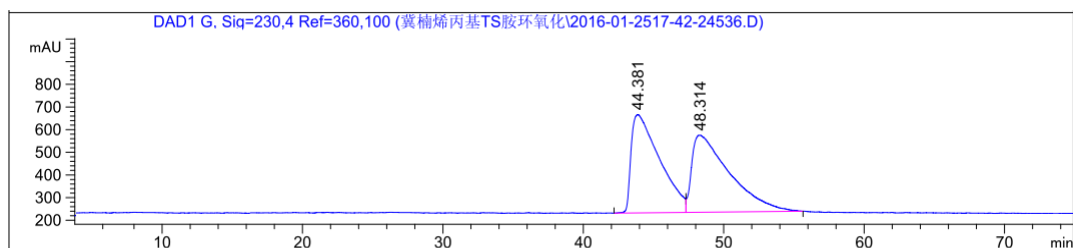
信号 3: DAD1 C, Sig=226.5,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.642	BB	0.8115	6.16978e4	1098.06287	95.7007
2	23.053	MM	0.8280	2771.73071	55.78875	4.2993

总量 : 6.44695e4 1153.85162



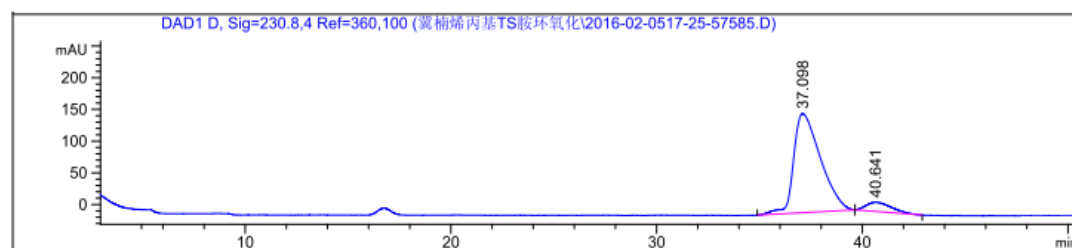
3i: HPLC: Chiralcel OD column, Hx/*i*-PrOH 95:5, 1.0 mL/min. t_{major} : 37.0 min;
 t_{minor} : 40.6 min. (83% ee)



信号 7: DAD1 G, Sig=230,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	44.381	BV	1.6744	6.12132e4	433.76071	48.9929
2	48.314	VB	2.1934	6.37297e4	340.22607	51.0071

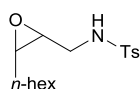
总量 : 1.24943e5 773.98679



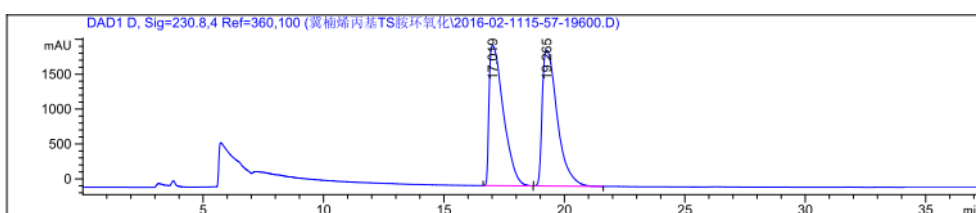
信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	37.098	BB	1.2881	1.41659e4	156.49516	91.9910
2	40.641	BB	1.0365	1233.32068	14.43939	8.0090

总量 : 1.53992e4 170.93455



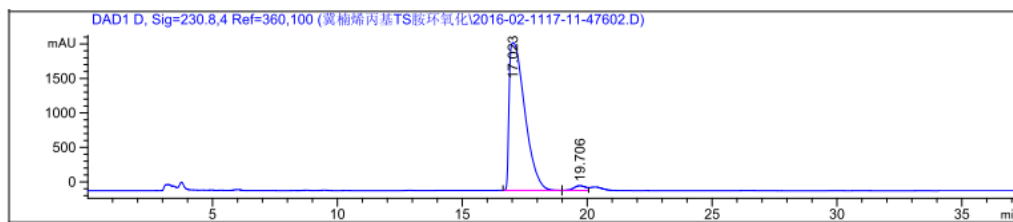
3j: HPLC: Chiralcel AD column, Hx/*i*-PrOH 90:10, 1.0 mL/min. t_{major} : 17.0 min;
 t_{minor} : 19.7 min. (95% ee)



信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.019	BB	0.5500	8.25080e4	2013.99878	49.4555
2	19.265	BB	0.6699	8.43247e4	1944.62024	50.5445

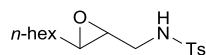
总量 : 1.66833e5 3958.61902



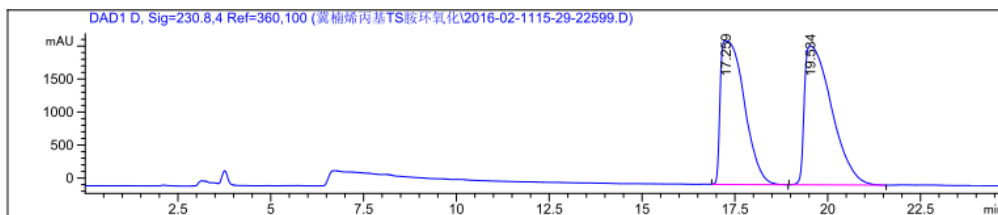
信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.023	BB	0.5593	9.27727e4	2141.87891	97.6343
2	19.706	BV	0.4996	2247.91187	68.71729	2.3657

总量 : 9.50206e4 2210.59620



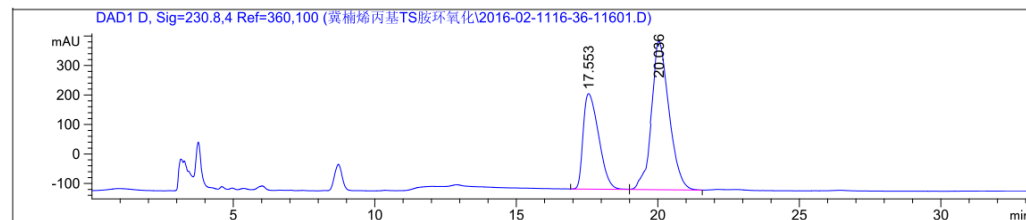
3k: HPLC: Chiralcel AD column, Hx/i-PrOH 90:10, 1.0 mL/min. t_{minor} : 17.5 min; t_{major} : 20.0 min. (31% ee)



信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.259	VB	0.5333	9.72655e4	2176.89307	47.6093
2	19.534	BB	0.6694	1.07034e5	2104.22632	52.3907

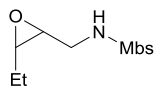
总量 : 2.04299e5 4281.11938



信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

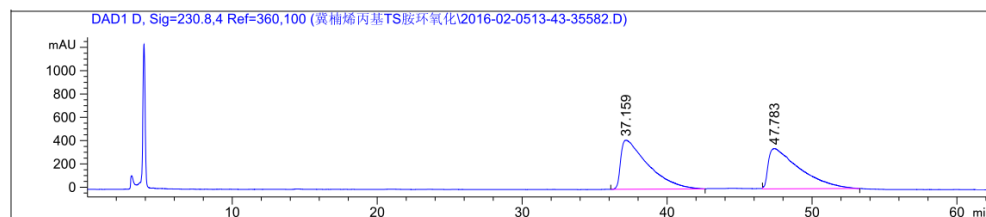
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.553	BV	0.5931	1.22922e4	323.66684	34.5931
2	20.036	VB	0.6747	2.32414e4	503.37552	65.4069

总量 : 3.55336e4 827.04236



3l: HPLC: Chiralcel OD column, Hx/*i*-PrOH 92:8, 1.0 mL/min. t_{major} : 38.7 min;

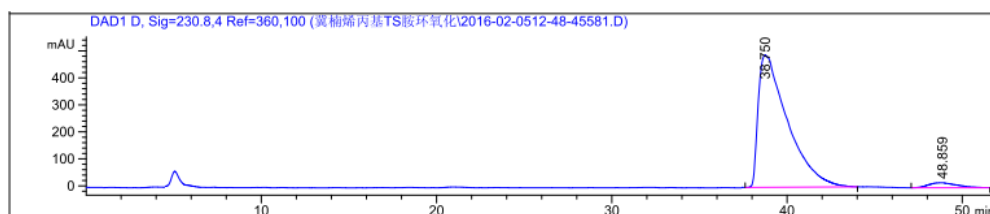
t_{minor} : 48.8 min. (93% ee)



信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	37.159	BV	1.7060	5.49178e4	420.42410	51.4306
2	47.783	VB	1.9793	5.18626e4	344.71631	48.5694

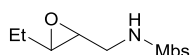
总量 : 1.06780e5 765.14041



信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

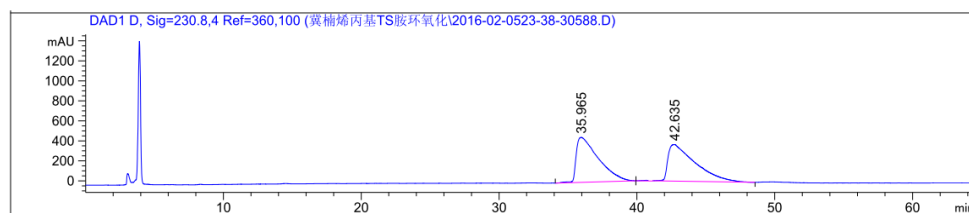
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	38.750	BB	1.5340	5.68979e4	489.54938	96.4906
2	48.859	BB	1.3644	2069.40405	18.50912	3.5094

总量 : 5.89674e4 508.05850



3m: HPLC: Chiralcel OD column, Hx/*i*-PrOH 92:8, 1.0 mL/min. t_{major} : 38.5 min;

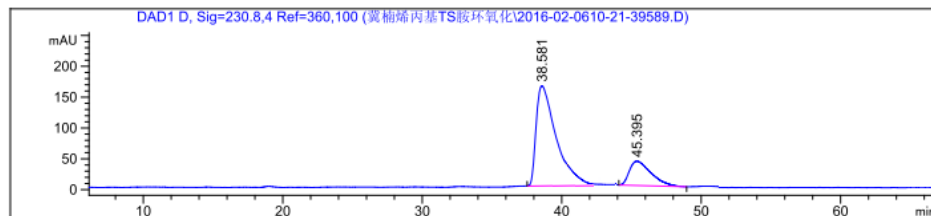
t_{minor} : 45.3 min. (55% ee)



信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	35.965	BB	1.4483	5.00309e4	448.89526	49.9440
2	42.635	BB	1.6532	5.01431e4	364.90359	50.0560

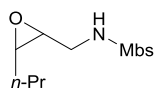
总量 : 1.00174e5 813.79886



信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

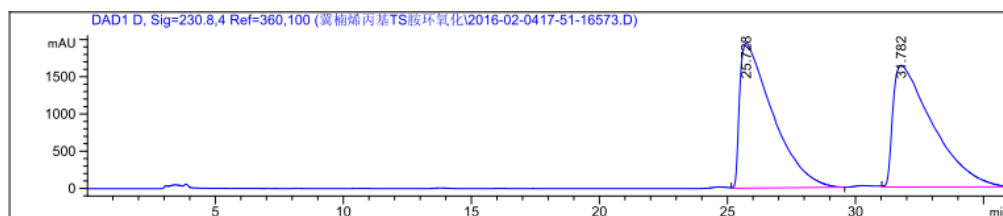
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	38.581	BV	1.3433	1.49183e4	162.16631	77.8312
2	45.395	BB	1.2927	4249.19189	39.32385	22.1688

总量 : 1.91675e4 201.49016



3n: HPLC: Chiralcel OD column, Hx/*i*-PrOH 90:10, 1.0 mL/min. t_{major} : 26.9 min;

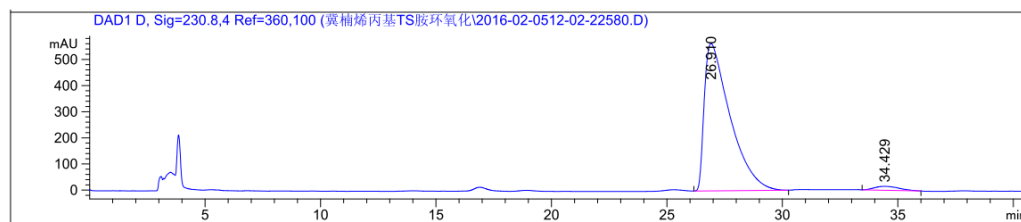
t_{minor} : 34.2 min. (95% ee)



信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	25.728	VB	1.1625	1.73947e5	1950.37793	49.5995
2	31.782	VBA	1.4140	1.76756e5	1634.04419	50.4005

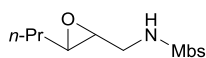
总量 : 3.50703e5 3584.42212



信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

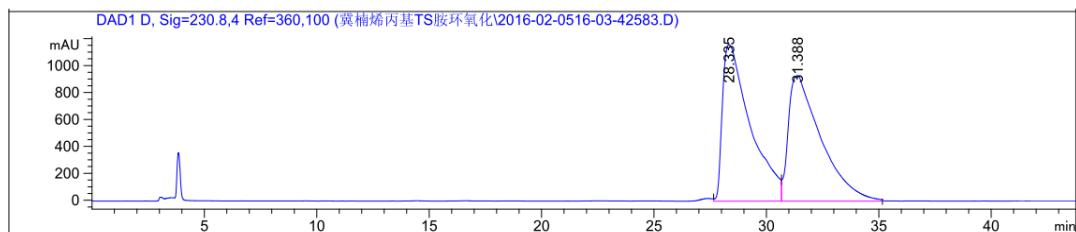
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	26.910	BB	1.1355	4.34891e4	564.03070	97.5543
2	34.429	BB	0.9332	1090.25793	14.87366	2.4457

总量 : 4.45794e4 578.90436



3o: HPLC: Chiralcel OD column, Hx/*i*-PrOH 90:10, 1.0 mL/min. t_{major} : 29.1

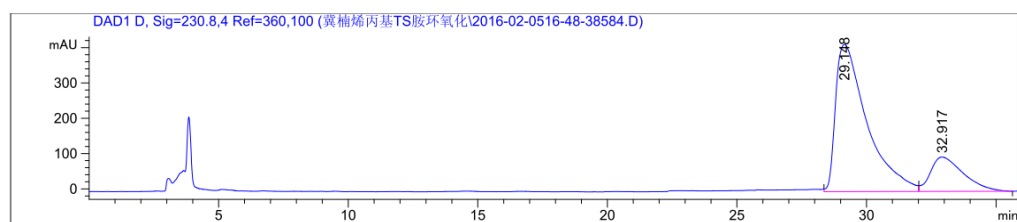
min; t_{minor} : 32.9 min. (61% ee)



信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	28.335	VV	1.1968	9.95446e4	1162.77612	51.4033
2	31.388	VV	1.3728	9.41094e4	931.38678	48.5967

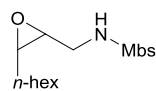
总量 : 1.93654e5 2094.16290



信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

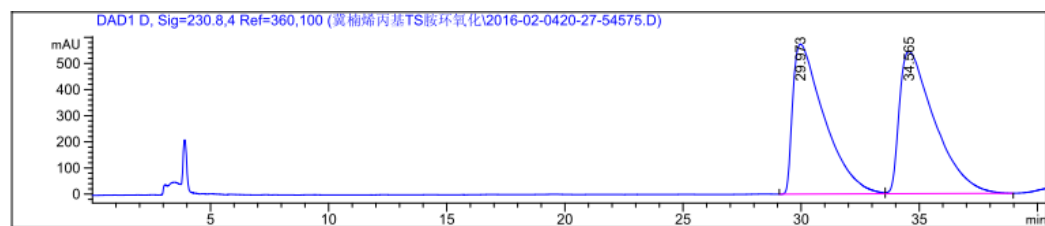
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	29.148	VV	1.2082	3.50669e4	417.39087	80.3051
2	32.917	VB	1.2603	8600.19824	97.38467	19.6949

总量 : 4.36671e4 514.77554



3p: HPLC: Chiralcel OD column, Hx/*i*-PrOH 92:8, 1.0 mL/min. t_{major} : 30.0 min;

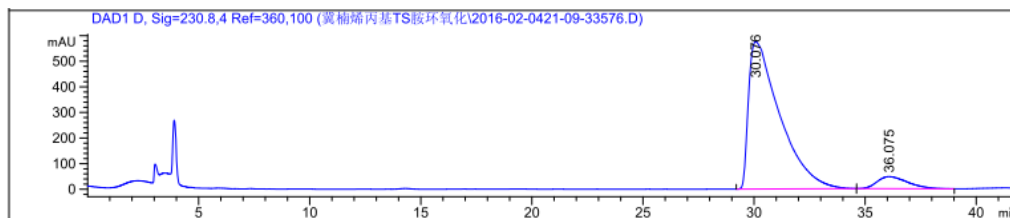
t_{minor} : 36.0 min. (85% ee)



信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	29.973	BV	1.2822	5.34407e4	573.99091	48.6215
2	34.565	VB	1.4760	5.64710e4	544.49329	51.3785

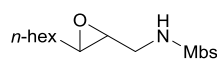
总量 : 1.09912e5 1118.48419



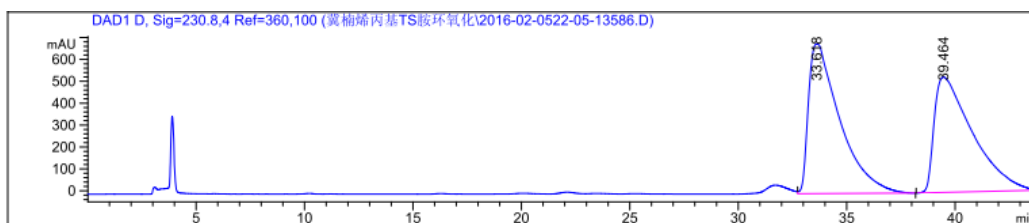
信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	30.076	BB	1.2960	5.62674e4	575.84167	92.6188
2	36.075	BB	1.3034	4484.16455	46.98800	7.3812

总量 : 6.07516e4 622.82967



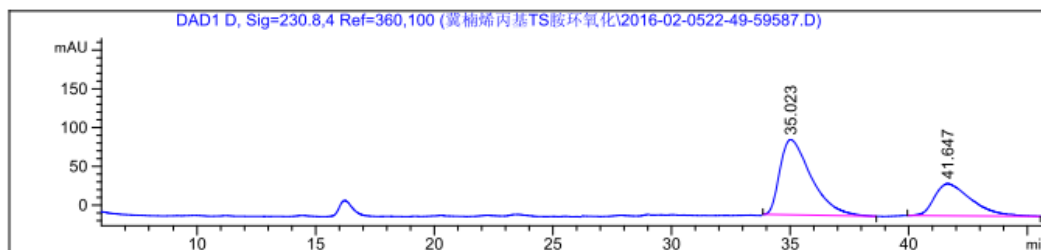
3q: HPLC: Chiralcel OD column, Hx/*i*-PrOH 92:8, 1.0 mL/min. t_{major} : 35.0 min; t_{minor} : 41.6 min. (37% ee)



信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	33.618	VB	1.3181	6.88399e4	684.05792	51.6084
2	39.464	BBA	1.7078	6.45491e4	526.71069	48.3916

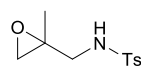
总量 : 1.33389e5 1210.76862



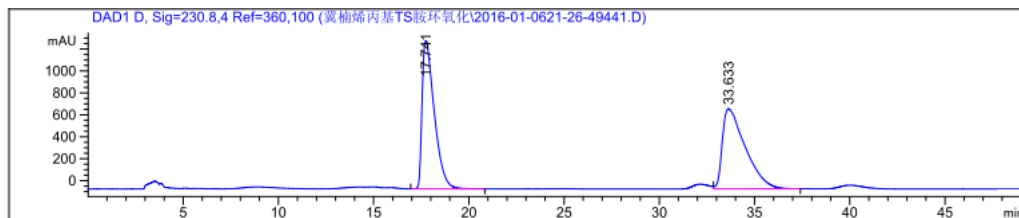
信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	35.023	BB	1.3195	6175.57861	96.77043	68.3982
2	41.647	BB	1.3167	2853.28711	41.55940	31.6018

总量 : 9028.86572 138.32983



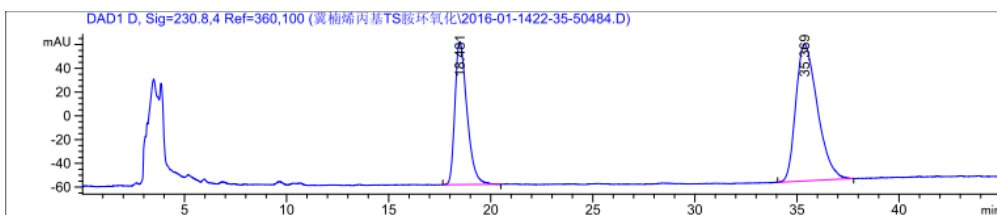
3r: HPLC: Chiralcel OD column, Hx/*i*-PrOH 90:10, 1.0 mL/min. t_{minor} : 18.4 min; t_{major} : 35.3 min. (29% ee)



信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.741	BB	0.6750	5.99314e4	1352.51636	49.5449
2	33.633	VB	1.1326	6.10324e4	730.57074	50.4551

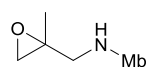
总量 : 1.20964e5 2083.08710



信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

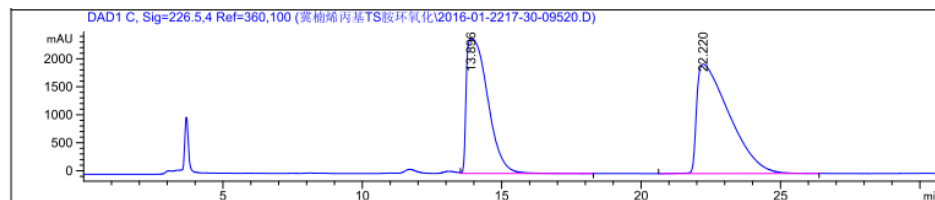
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.481	MM	0.6432	5035.13330	130.47516	35.0577
2	35.369	BB	1.1017	9327.29492	127.47256	64.9423

总量 : 1.43624e4 257.94772



3s: HPLC: Chiralcel OD column, Hx/*i*-PrOH 80:20, 1.0 mL/min. t_{minor} : 14.4 min;

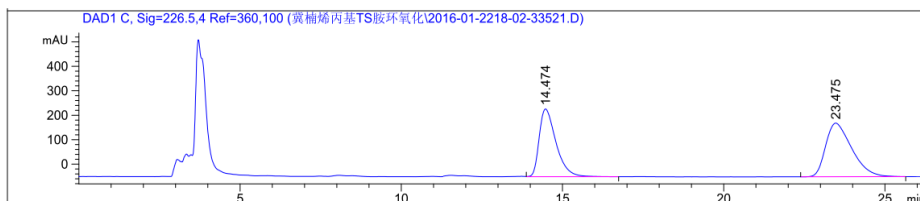
t_{major} : 23.4 min. (17% ee)



信号 3: DAD1 C, Sig=226.5,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.896	VB	0.6772	1.27927e5	2410.44922	44.7059
2	22.220	BB	1.0413	1.58225e5	1956.94714	55.2941

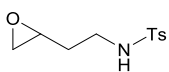
总量 : 2.86152e5 4367.39636



信号 3: DAD1 C, Sig=226.5,4 Ref=360,100

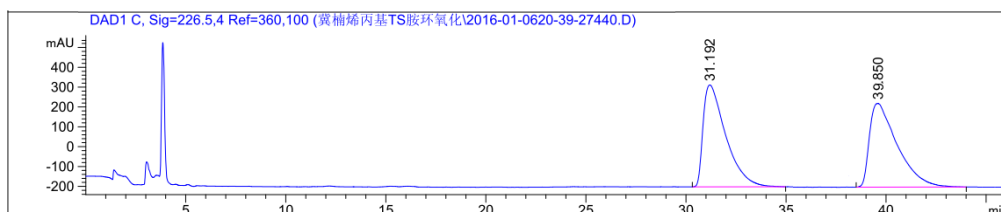
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.474	MM	0.5464	8693.60645	265.20010	41.3537
2	23.475	BB	0.8668	1.23290e4	219.65356	58.6463

总量 : 2.10226e4 484.85367



3t: HPLC: Chiralcel OD column, Hx/i-PrOH 90:10, 1.0 mL/min. t_{major} : 35.6 min;

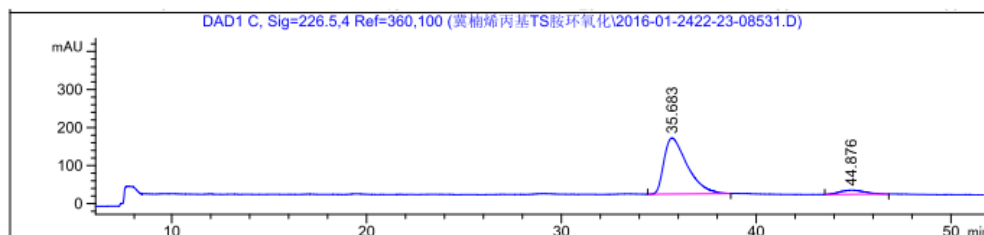
t_{minor} : 44.8 min. (85% ee)



信号 3: DAD1 C, Sig=226.5,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	31.192	BB	1.1121	4.04063e4	513.46100	49.8223
2	39.850	VB	1.1877	4.06945e4	421.76215	50.1777

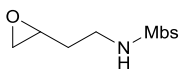
总量 : 8.11007e4 935.22314



信号 3: DAD1 C, Sig=226.5,4 Ref=360,100

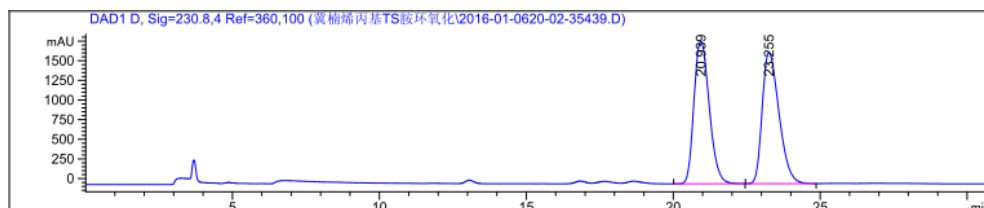
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	35.683	BB	1.2184	1.22091e4	147.38626	92.6425
2	44.876	BB	1.0428	969.62262	10.93140	7.3575

总量 : 1.31787e4 158.31766



3u: HPLC: Chiralcel AD column, Hx/i-PrOH 80:20, 1.0 mL/min. t_{minor} : 21.8 min;

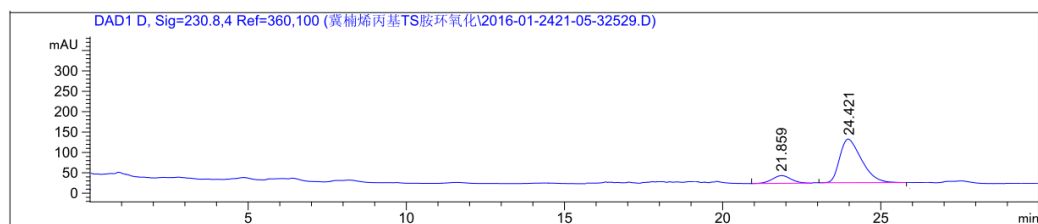
t_{major} : 24.4 min. (73% ee)



信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.939	BB	0.5684	6.56982e4	1814.38025	49.7877
2	23.255	BB	0.6204	6.62585e4	1671.67310	50.2123

总量 : 1.31957e5 3486.05334



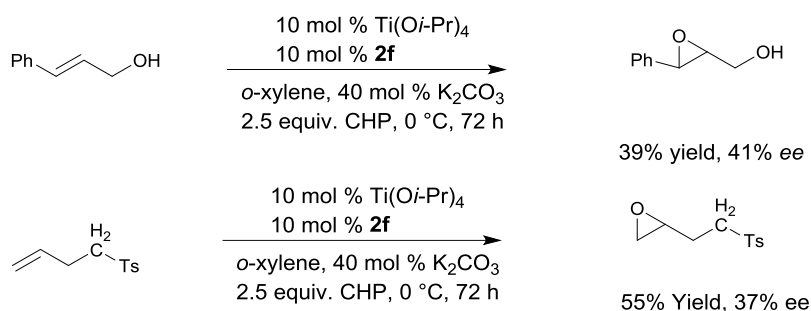
信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	21.859	BB	0.6199	782.87463	18.95262	13.2329
2	24.421	BB	0.6857	5133.25781	111.80004	86.7671

总量 : 5916.13245 130.75266

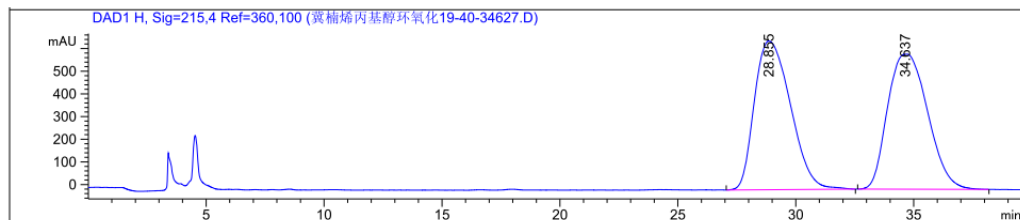
11.Epoxidation of allylic alcohol and allylic sulfone

The allylic alcohol and allylic sulfone had been also tested under the optimum conditions: 10% Ti(Oi-Pr)₄, Schiff base **2f** (10 mol%), K₂CO₃ (40 mol%), CHP (2.5 equiv.), 0°C and *o*-xylene without further methodological study. The allylic alcohol and allylic sulfone epoxides had been achieved by 39% yield, 41% ee and 55% yield, 37% ee respectively.



Scheme 2. Epoxidation of allylic alcohol and allylic sulfone

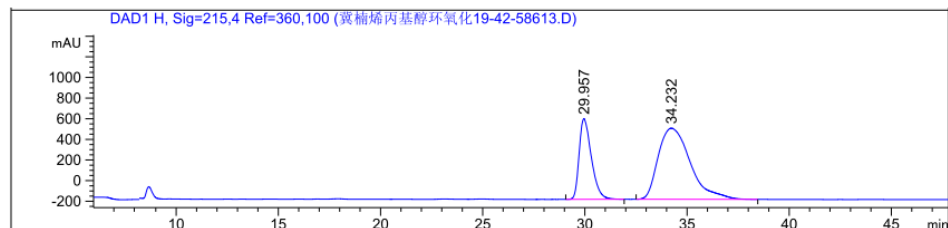
c1ccc(cc1)C1OC1CO HPLC: Chiralcel OD column, Hx/*i*-PrOH 95:5, 1.0 mL/min. *t*_{minor}: 29.9 min; *t*_{major}: 34.2 min. (41% ee)



信号 8: DAD1 H, Sig=215,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	28.855	BB	1.5539	6.96930e4	655.74738	49.7894
2	34.637	BB	1.5251	7.02825e4	595.41052	50.2106

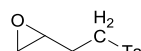
总量 : 1.39975e5 1251.15790



信号 8: DAD1 H, Sig=215,4 Ref=360,100

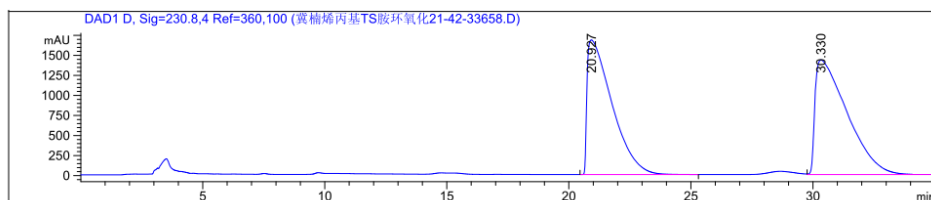
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	29.957	BB	0.6344	3.24877e4	782.52039	29.9330
2	34.232	BB	1.5316	7.51513e4	689.48456	70.0670

总量 : 1.07639e5 1472.00494



HPLC: Chiralcel OD column, Hx/*i*-PrOH 85:15, 1.0 mL/min. t_{minor} : 22.0 min; t_{major} :

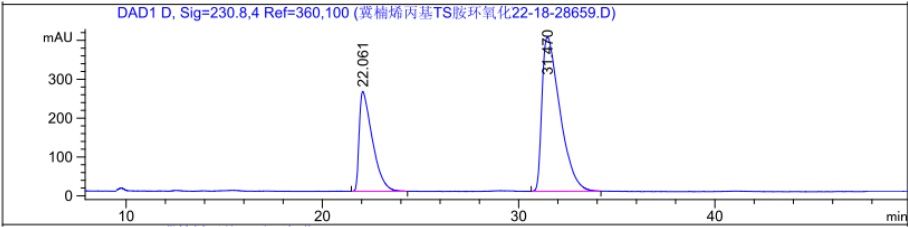
31.4 min. (37% ee)



信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.927	BB	0.9023	1.18666e5	1679.61548	47.6053
2	30.330	VBA	1.1819	1.30605e5	1429.58350	52.3947

总量 : 2.49271e5 3109.19897



信号 4: DAD1 D, Sig=230.8,4 Ref=360,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	22.061	BB	0.7003	1.19563e4	257.22943	31.7769
2	31.470	BB	0.9466	2.52682e4	396.95706	68.2231

总量 : 3.72244e4 654.18649